APR 1 6 1932

U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 8 MARCH, 1932 No. 3

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
416.	Heat of vaporization of water at 50°, 70°, and 90° C. E. F. Fiock and D. C. Ginnings	321
417.	Note on international comparison of X-ray standards. Lauriston S. Taylor	325
418.	The course of the oxidation of the aldose sugars by bromine water. H. S. Isbell and C. S. Hudson	327
419.	Fluctuations of the rate of emissions of α particles for weak sources and large solid angles. L. F. Curtiss	339
420.	Gases obtained from commercial feldspars heated in vacuo. G. R. Shelton and H. H. Holscher	347
421.	Experiments on the emission and absorption of radiation by metallic silver. F. L. Mohler	357
422.	Accelerated weathering tests of soldered and tinned sheet copper. Peter R. Kosting	365
423.	The chromium oxide and the vanadium oxide band spectra. W. F. C. Ferguson	381
424.	Air density corrections for X-ray ionization chambers. Lauriston S. Taylor and George Singer	385
425.	The arc spectrum of phosphorus. C. C. Kiess	393
426.	Some physical properties of levulose and its estimation by copper reduction methods. Richard F. Jackson and Joseph A. Mathews	403

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

October, 1931 (Vol. 7, No. 4)

RP361. Relation between the twist and certain properties of rayon yarns. Homer A. Hamm and Richard S. Cleveland. Price, 5 cents.

RP362. The hydrolysis of chestnut and quebracho tanned leathers by sulphuric acid. E. L. Wallace. Price, 5 cents.

RP363. Correlation of certain soil characteristics with pipe line corrosion. I. A. Denison. Price, 5 cents.

RP364. Further description and analysis of the first spectrum of krypton. Wm. F. Meggers, T. L. deBruin, and C. J. Humphreys. Price, 10 cents.

RP365. A correlated color temperature for illuminants. Raymond Davis. Price, 10 cents.

RP366. Quartz plate mountings and temperature control for piezo oscillators. Vincent E. Heaton and E. G. Lapham. Price, 10 cents.

RP367. An improved audio-frequency generator. E. G. Lapham. Price, 10 cents.

RP368. The porosity of electroplated chromium coatings. W. Blum, W. P. Barrows, and A. Brenner. Price, 10 cents.

RP369. The use of saturated ammonium chloride in the elimination of contact potentials. C. N. Murray and S. F. Acree. Price, 5 cents.

RP370. A balanced thermocouple and filter method of ultra-violet radiometry, with practical applications. W. W. Coblentz, R. Stair, and J. M. Hogue. Price, 10 cents.

RP371. Radiation from probe surfaces bombarded by electrons. F. L. Mohler and C. Boeckner. Price, 5 cents.

November, 1931 (Vol. 7, No. 5)

RP372. Highly purified wood fibers as paper-making material. Royal H. Rasch, Merle B. Shaw, and George W. Bicking. Price, 15 cents.

RP373. Preliminary note on an automatic recorder giving a continuous height record of the Kennelly-Heaviside layer. T. R. Gilliland and G. W. Kenrick.

RP374. The relative spectral energy distribution and correlated color temperature of the N. P. L. white-light standard. Raymond Davis and K. S. Gibson. Price, 5 cents.

RP375. Isolation and determination of methylcyclopentane in a midcontinent petroleum. Mildred M. Hicks-Bruun and Johannes H. Bruun. Price, 5 cents.

RP376. The photographic emulsion; the silver ion-gelatin equilibrium. Burt H. Carroll and Donald Hubbard. Price, 5 cents.

RP377. A general formula for the computation of colorimetric purity. Deane B. Judd.

RP378. Variation of photographic sensitivity with different light sources. Raymond Davis and Gerald Kent Neeland. Price, 5 cents.

RP379. Laboratory rectifying stills of glass. Johannes H. Bruun and Sylvester T. Schicktanz. Price, 20 cents.

RP380. The use of zinc oxide in determinations of cobalt and manganese. James I. Hoffman. Price, 5 cents.

RP381. The decomposition of tricalcium silicate in the temperature range, 1,000°–1,300° C. E. T. Carlson. Price, 5 cents.

RP382. The determination of the coefficient of cubical expansion of solid benzoic acid by means of a gas-filled dilatometer. E. R. Smith. Price, 5 cents.

RP383. Isolation of normal nonane from a midcontinent petroleum. Joseph D. White and F. W. Rose, jr. Price, 5 cents.

RP384. The analysis of cyanide silver plating solutions. R. M. Wick. Price, 10 cents.

RP385. Silvering and evacuating pyrex Dewar flasks. R. B. Scott, J. W. Cook, and F. G. Brickwedde. Price, 5 cents.

RP386. The relation of torque to tension for thread-locking devices. H. L. Whittemore, G. W. Nusbaum, and E. O. Seaquist. Price, 30 cents.

Research papers, where price is given, are already available, and others will be available in the near future, as separates for purchase from the Superintendent of Documents, United States Government Printing Office, Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
R. P. LAMONT, Secretary
BUREAU OF STANDARDS
GEORGE K. BURGESS, Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

March, 1932
Vol. 8, No. 3

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1932

For sale by the Superintendent of Documents, Washington, D. C. • • • Price 40 cents; $3 Per Year on Subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH see pages 2 and 3 of the cover

RP416

HEAT OF VAPORIZATION OF WATER AT 50°, 70°, AND 90° C.

By E. F. Fiock and D. C. Ginnings

ABSTRACT

The values of the heat of vaporization of water at 50°, 70°, and 90° C. have been determined as 2,381.6, 2,333.6, and 2,283.4 international joules per gram. These results were obtained subsequent to the publication of a detailed report on calorimetric determinations of thermal properties of saturated water and steam. The measured values below 100° are in excellent agreement with those obtained by extrapolation from the measurements above 100° C.

Thermal properties of saturated water and steam in the range from 0° to 270° C., as measured at this bureau, have already been published.[1] The determinations of heat of vaporization given before extended from 100° to 270° C. Since the publication of the first paper it has been possible to extend the measurements of heat of vaporization down to 50° C. These measurements have been carried out under the direction of N. S. Osborne and H. F. Stimson. This brief report is given as a supplement to the previous detailed description. The apparatus, manipulation, notation, and reduction of the data are essentially unchanged.

The results of the more recent experiments are given in detailed form in Table 1.

[1] B. S. Jour. Research, vol. 5 (RP209), pp. 411–480, 1930.

TABLE 1.—*Principal data from γ experiments below 100° C.*

$$\gamma_1=\frac{1}{\Delta M}\left\{Q_E+Q_P+Q_L-[Z+M_2\alpha]_1^2\right\}+\frac{\Delta H'}{\Delta\theta}(\theta_1-\theta_m)$$

Experiment No.	Date	Initial temperature θ_1	Final temperature θ_2	Total time of experiment	Mass of vapor removed ΔM	Mass of water remaining M_2	Total electric energy Q_E	Pump energy Q_P	Heat leak Q_L	Energy correction for final temperature difference $-[Z+M_2\alpha]_1^2$	Entire energy added	Entire energy per gram γ_1	γ_θ Corrected to even temperature	Residual $\gamma_\theta-\gamma_m$
		°C.	°C.	Minutes	g	g	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules	Int. joules/g	Int. joules/g	Int. joules/g
290–A	Aug. 7, 1930	50.074	50.084	42	18.721	391.0	44,446.3	166.7	0.0	−24.4	44,588.6	2,381.9	2,381.7	−0.1
290–B	do	50.080	50.088	30	13.478	366.5	32,015.9	119.1	.0	−19.3	32,115.7	2,382.8	2,383.0	1.0
290–C	do	50.068	50.076	40	17.971	330.5	42,651.4	158.8	.0	−16.7	42,793.5	2,381.2	2,381.4	−.6
291–A	Aug. 8, 1930	50.043	50.049	41	18.391	285.4	43,650.5	162.8	.0	−13.9	43,799.4	2,381.6	2,381.7	−.3
291–B	do	50.049	50.049	40	17.938	267.5	42,556.4	158.8	.0	1.4	42,716.6	2,381.3	2,381.4	−.6
291–C	do	50.049	50.033	40	17.935	249.5	42,532.2	158.8	.0	29.9	42,720.9	2,382.0	2,382.1	.1
291–D	do	50.033	50.040	40	17.910	231.6	42,519.1	158.8	.0	−12.2	42,665.7	2,382.2	2,382.3	.3
291–E	do	50.040	50.028	40	17.919	213.7	42,509.2	158.8	.0	21.5	42,689.5	2,382.4	2,382.4	.4
291–F	do	50.028	50.023	40	17.910	195.8	42,489.0	158.8	.0	9.0	42,656.8	2,381.7	2,381.8	−.2
91–G	do	50.023	50.045	41	18.323	177.5	43,528.7	162.8	.0	−37.1	43,654.4	2,382.5	2,382.5	.5
Even temperature 50° C.		Z_{50}=856 int. joules per ° C.			α_{50}=4.170 int. joules per g ° C.		Mean value of $\gamma_\theta=\gamma_m$=2,382.0 int. joules per g							
292–A	Aug. 11, 1930	70.063	70.062	30	15.235	391.5	35,450.0	111.9	.0	2.8	35,564.7	2,334.4	2,334.6	.7
292–B	do	70.062	70.077	35	17.745	373.8	41,324.8	130.6	5.5	−37.3	41,423.6	2,334.4	2,334.5	.6
292–C	do	70.061	70.066	45	22.810	333.6	53,066.7	167.9	2.8	−11.4	53,226.0	2,333.4	2,333.6	−.3
292–D	do	70.064	70.070	32	16.204	299.2	37,701.3	119.4	1.1	−13.3	37,808.5	2,333.3	2,333.4	−.5
292–E	do	70.056	70.059	32	16.179	267.8	37,627.1	119.4	.2	−5.3	37,741.4	2,332.7	2,332.9	−1.0
292–F	do	70.059	70.063	30	15.245	252.5	35,467.9	111.9	.7	−7.9	35,572.6	2,333.4	2,333.5	−.4
292–G	do	70.063	70.064	30	15.239	237.3	35,464.2	111.9	−1.8	−2.3	35,572.0	2,334.3	2,334.4	.5
293–A	Aug. 12, 1930	70.021	70.014	25	17.852	385.5	41,567.3	93.3	−.7	15.9	41,675.8	2,334.5	2,334.6	.7
293–B	do	70.014	70.006	25	17.857	367.6	41,555.9	93.3	−.7	19.9	41,668.4	2,333.4	2,333.5	−.4
293–C	do	70.006	70.010	25	17.834	349.8	41,548.1	93.3	−.5	−9.0	41,631.9	2,334.4	2,334.4	.5
293–D	do	70.010	70.012	20	14.267	335.5	33,233.7	74.6	.2	−3.7	33,304.8	2,334.4	2,334.4	.5
293–E	do	70.008	70.006	20	14.270	306.9	33,225.1	74.6	.0	4.4	33,304.1	2,333.8	2,333.9	.0
293–F	do	70.006	70.003	20	14.275	292.7	33,222.1	74.6	.0	6.6	33,303.3	2,333.0	2,333.0	−.9
293–G	do	70.003	70.012	20	14.259	278.4	33,218.7	74.6	.2	−18.1	33,275.4	2,333.6	2,333.6	−.3
293–H	do	70.012	70.008	20	14.264	264.1	33,214.9	74.6	−.2	4.5	33,293.8	2,334.1	2,334.1	.2

293–G															−.3
293–H	do	70.013													−.2
293–I	do	70.008													−.6
293–J	do	70.000													−.2
293–K	do	70.008													−.2
	do	70.000													
	Even temperature 70° C.	Z_{70}=869 int. joules per ° C.		σ_{70}=4.169 int. joules per g° C.			Mean value of $\gamma_{\theta}=\gamma_{\infty}$=2,333.9 int. joules per g								
295–A	Aug. 16, 1930	89.925	20	16.802	312.5	38, 298.0	70.6	.7	14.6	38, 383.9	2, 284.3	2, 284.2	.5
295–B	do	89.918	44	16.802	275.6	84, 102.4	155.3	.6	84, 259.2	2, 283.9	2, 283.7	.0	
295–C	do	89.918	20	16.760	285.8	38, 224.3	70.6	.0	−11.8	38, 283.1	2, 284.2	2, 284.0	.3
295–D	do	89.924	26	21.782	237.1	49, 671.0	91.8	.2	7.4	49, 770.4	2, 284.9	2, 284.7	1.0
295–E	do	89.920	20	16.760	220.3	38, 191.9	70.6	−.5	−.4	38, 261.6	2, 282.9	2, 282.7	−1.0
295–F	do	89.920	27	22.602	197.7	51, 535.4	95.3	−1.1	8.3	51, 637.9	2, 284.7	2, 284.4	.7
295–G	do	89.916	20	16.753	180.9	38, 169.9	70.6	.0	−1.2	38, 239.3	2, 282.5	2, 282.3	−1.4
	Even temperature 90° C.	Z_{90}=885 int. joules per ° C.		σ_{90}=4.168 int. joules per g° C.			Mean value of $\gamma_{\theta}=\gamma_{\infty}$=2,283.7 int. joules per g								

Table 2 shows the reduced results of the experiments at low temperatures. The values of β in column 3 were calculated from the equation $\beta=\frac{Lu}{u'-u}$, using the values of u' given by Keyes and Smith.[2]

TABLE 2.—*Heat of vaporization (L) of water at 50°, 70°, and 90° C.*

Temperature θ	γ observed	β calculated	L	
			Observed	Calculated
°C.	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
50	2,382.0	0.2	2,381.8	2,381.6
70	2,333.9	.5	2,333.4	2,333.6
90	2,282.7	1.0	2,282.7	2,283.4

NOTE.—The values of L shown in column 5 were calculated from the equation

$$L=0.002562(374-\theta)^2-5.883(374-\theta)+249.9(374-\theta)^{1/2}-113(374-\theta)^{1/4}.$$

This equation, which was fitted to the observed values of heat of vaporization above 100°, holds equally well for the observations down to 50° C.

WASHINGTON, January 6, 1932.

[2] Mechanical Engineering, vol. 53, pp. 132-135; 1931.

NOTE ON INTERNATIONAL COMPARISON OF X-RAY STANDARDS

By Lauriston S. Taylor

A recent paper [1] gave a description of comparisons of the Bureau of Standards X-ray ionization standard with that of the National Physical Laboratory, Physikalisch-technische Reichsanstalt, and Le Service d'Etalonnage de l'Hôpital St. Antoine. In these comparisons it was necessary in all cases to make corrections for the absorption of X rays in air, for which absorption coefficients were obtained by extrapolation from available data. These coefficients are, as pointed out, uncertain.

Unfortunately, corrections for this paper, suggested by Doctor Kaye, were received after it was too late to insert them. He informs us that their recent determinations of the air absorption correction under the conditions used in the comparisons gives values somewhat different from those used in the published paper. For 110 kv unfiltered radiation Doctor Kaye finds a correction of 2.2 per cent as against 1.5 per cent used in the published paper. For 143 kv, 1.4 mm copper, his correction agreed with the published value. Applying the first correction raises the values of the N. P. L. determination by approximately 0.7 per cent.

When Kaye's values are used, column 11, Table 3 of the published paper becomes:

	Per cent
Average difference of intact systems	−1. 0
Corrected for compensator differences	+. 5
Average difference when using the same diaphragms	−1. 9
Corrected for compensator differences	−. 4

The resulting N. P. L. values for the magnitude of the roentgen, as given in Table 9, column 4, are:

1.005 when corrected for diaphragm differences.
.996 when using the same diaphragm on both chambers.
1.0005 when averaging all readings taken.

We would also call attention to an error, page 16, line 3 under Table 3. The sentence should read: "Runs 1 and 3 are straightforward comparisons; run 2 was made with the tube diaphragm increased in diameter from 12 to 30 mm; * * *."

WASHINGTON, January 8, 1932.

[1] L. S. Taylor, B. S. Jour. Research, vol. 8 (RP397), pp. 9-24, 1932.

THE COURSE OF THE OXIDATION OF THE ALDOSE SUGARS BY BROMINE WATER

By H. S. Isbell and C. S. Hudson

ABSTRACT

The optical rotation of a buffered glucose solution upon bromine oxidation rises to a point which corresponds approximately with the rotation of the delta gluconic lactone; then the rotation decreases to a minimum value at a rate corresponding to the hydrolysis of the delta lactone; and finally the rotation slowly increases to a point corresponding to the equilibrium rotation of gluconic acid. These changes agree qualitatively with the hypothesis that the delta gluconic lactone is formed in solution immediately after the oxidation of the sugar by bromine water. Apparently the 1, 5 ring form of glucose is oxidized directly to the 1, 5 gluconic lactone, but the authors believe that further data must be obtained before this mechanism is definitely established.

The oxidation of various sugars was followed by the same method and similar changes were observed which indicate that the aldose sugars in general are oxidized by bromine water in slightly acid solution to the delta lactones rather than to the sugar acids as previously believed.

CONTENTS

	Page
I. Introduction	327
II. Bromine oxidation of glucose	328
III. Bromine oxidation of various sugars	331
1. Oxidation of *d*-galactose	332
2. Oxidation of *l*-arabinose	333
3. Oxidation of *d*-xylose	333
4. Oxidation of lactose	334
IV. Experimental details	335

I. INTRODUCTION

The oxidation of the aldose sugars to monobasic acids by bromine water, a classical reaction which was originally introduced by H. Kiliani,[1] has been considered as evidence for the aldehydic structure for glucose and related sugars. The mechanism of the reaction has been explained on the hypothesis that in an aqueous solution of glucose an aldehyde tautomer exists in small quantity in equilibrium with the normal form. As this aldehyde form is used up by oxidation the equilibrium disturbance causes a new portion to be formed; finally, all the sugar reacts as an aldehyde.[2, 3, 4, 5]

$$\underset{\text{Aldose}}{CH_2OH\,(CHOH)_4.CHO} + Br_2 + H_2O \rightarrow \underset{\text{Aldonic acid}}{CH_2OH\,(CHOH)_4.COOH} + 2HBr$$

[1] H. Kiliani, Ann., vol. 205, p. 182, 1880; also Kiliani and Kleeman, Ber., vol. 17, p. 1298, 1884.
[2] Pringsheim, "Zuckerchemie," Leipzig, p. 8, 1925.
[3] Crammer, "Les Sucres," Gaston Doin & Co., Paris, p. 22, 1927.
[4] Armstrong, "The Carbohydrates and the Glucosides," Longmans, Green & Co., London, p. 67, 1924.
[5] Haworth, "Constitution of Sugars," Edward Arnold & Co., London, p. 4, 1929.

This concept is based upon the fact that when 1 molecule of bromine reacts with 1 molecule of glucose the final products which have been isolated are 2 equivalents of hydrogen bromide and 1 molecule of gluconic acid. The isolation of these products does not determine the mechanism of the reaction because the sugar after oxidation may pass through a number of steps prior to the separation of the final products. This is particularly true in regard to the sugar acids as they are interconvertible with their lactones. In 1914 Nef [6] showed that gluconic acid forms two lactones rather than one. The second lactone he called a beta lactone, while the one previously known was considered as a gamma lactone; Nef's beta lactone is now believed to be a 1, 5 or delta lactone. The two lactones contain five and six membered oxygen rings in which respect they are analogous to the gamma and the normal forms of glucose. A freshly prepared aqueous solution of gluconic acid on standing forms an equilibrium between the acid and the two lactones. As shown by Levene and Simms [7] the delta lactone is formed rapidly while the gamma lactone is formed more slowly. By utilization of the different rates of formation either lactone may be separated at will. In the past the sugars have been regarded as being oxidized to the acids, the lactones being secondary products. It will be shown in the next paragraph that this fundamental concept must be altered in order to account for the experimental facts which are given.

II. BROMINE OXIDATION OF GLUCOSE

In a previous paper [8] the authors give an improved method for the preparation of aldonic acids which differs from previous methods in that during the oxidation of the sugar with bromine water a slightly acid reaction is maintained by means of a buffer. The reaction is rapid and nearly quantitative and hence it is possible to follow the course of the reaction by the optical rotation of the solution. When the reaction was followed in that manner a series of peculiar changes in optical rotation was observed. As illustrated in Curve I of Figure 1 the specific rotation of a buffered solution of glucose on oxidation increases in a few minutes to a maximum value, then decreases rapidly to a minimum and thereafter slowly increases and finally becomes constant.

When the oxidation is interrupted by removing the free bromine a mutarotation of the solution occurs. If the bromine is removed with sodium thiosulphate the mutarotation which follows is very rapid, as illustrated in Curve III of Figure 1, but if the bromine is removed without altering the acidity of the solution the specific rotation changes more slowly, as in Curve II. This may be accomplished by shaking the solution with olive oil. Since the bromine combines directly with the oil there are no objectionable by-products and no marked changes in acidity. If the bromine is removed with olive oil shortly after the specific rotation of the original oxidation mixture reaches a maximum, the rotation of the resulting solution decreases to a minimum and thereafter slowly rises to a constant value. These changes are entirely different from the changes characteristic of a

[6] Nef, Ann., vol. 403, p. 325, 1914.
[7] Levene and Simms, J. Biol. Chem., vol. 65, p. 31, 1925.
[8] C. S. Hudson and H. S. Isbell, J. Am. Chem. Soc., vol. 51, p. 2225, 1929; also in B. S. Jour. Research, vol. 3, p. 57, 1929.

gluconic acid solution. The specific rotation of a freshly prepared solution of gluconic acid (Curve IV, fig. 2) decreases from a negative value to zero, and finally becomes positive, and thereafter increases very slowly. Inasmuch as the specific rotation of gluconic acid is less than that of any known form of glucose if gluconic acid were formed initially the specific rotation would decrease rather than increase. The initial rise in the optical rotation of the solution of glucose on bromine oxidation shows that gluconic acid *is not the* primary product of the oxidation of glucose in acid solution. As a consequence, we must seek a new interpretation for the mechanism of this important reaction. With the experimental conditions used in the reaction under discussion a certain ring form of the sugar

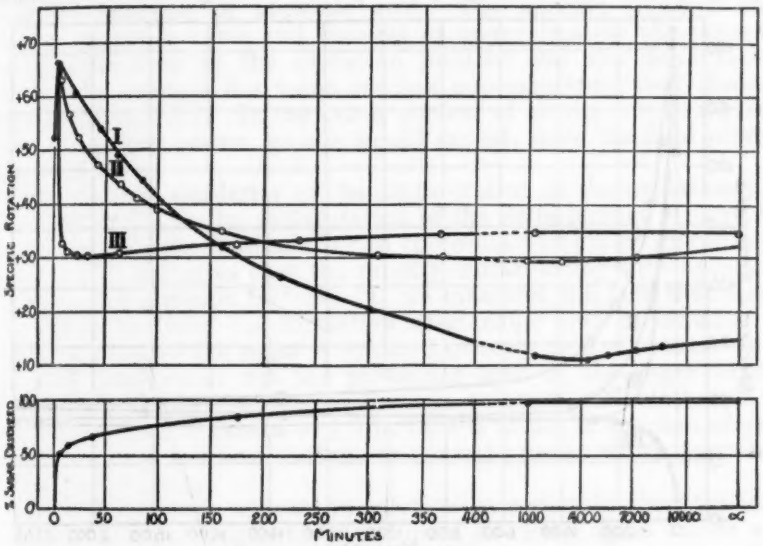


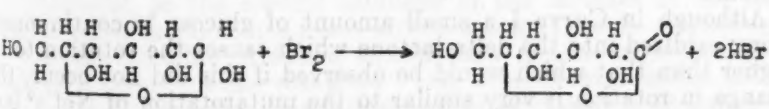
FIGURE 1.—*Bromine oxidation of glucose*

I, changes in the specific rotation of the sugar solution during oxidation.

II, changes in the specific rotation of a portion of the solution after interrupting the oxidation by removing the free bromine with olive oil.

III, changes in the specific rotation of a portion of the solution after removing the free bromine with sodium thiosulphate.

might be oxidized rather than the hypothetical aldehydic form. If the sugar ring is not broken a gluconic lactone would be formed directly as indicated by the following equation:



According to this concept the oxidation of glucose by bromine consists in the transfer of each of the two hydrogen atoms associated with the terminal carbon atom in a molecule of glucose to a molecule of bromine, giving a net result of 1 molecule of gluconic lactone and 2 molecules of hydrogen bromide. If the normal form of glucose (1,5) were oxidized in this manner the delta or 1,5 gluconic lactone would be formed. This would explain the changes in rota-

tion observed during the bromine oxidation of the sugar. Thus, if the oxidation product is the delta lactone the initial rise in specific rotation is caused by its formation, the subsequent rapid decrease in rotation being due to its hydrolysis to gluconic acid, the hydrolysis proceeding until a quasi equilibrium is established between the delta lactone and the acid, thus accounting for the minimum value, and simultaneously a second or gamma lactone is formed very slowly. The formation of the second lactone, continuing long after equilibrium is established between the delta lactone and the acid, adequately explains the slow rise in rotation.

A comparison of the changes in optical rotation of glucose on bromine oxidation, of gluconic acid, and the delta lactone, is given in Figure 2, which shows graphically the close agreement in rotation

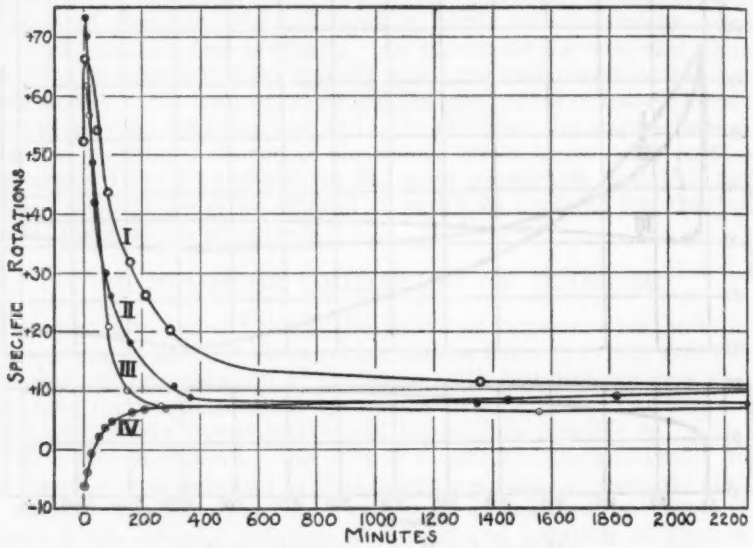


FIGURE 2.—*Curves showing a comparison in the specific rotation of the oxidation product from glucose with gluconic acid and its delta lactone*

I, a buffered glucose solution upon bromine oxidation (Table 1).

II, rotation of the oxidation product from glucose after bromine oxidation in which further oxidation was stopped by removing the excess bromine (sample A, Table 2).

III, mutarotation of the delta gluconic lactone (Nef).

IV, mutarotation of a buffered solution of gluconic acid (Table 5).

and reaction rates of the oxidation product with the delta gluconic lactone.

Although in Curve I a small amount of glucose is continuously being oxidized into the delta lactone which causes the rotation to be higher than that which would be observed if this did not occur, the change in rotation is very similar to the mutarotation of Nef's[9] lac-

[9] Nef, Ann., vol. 403, p. 325, 1914. The following data are given: 0.8010 g of the "*β*" gluconic lactone was dissolved in 19.3220 g of water and the following rotations were read in a 1 dm tube at 20°C.; 12 minutes after solution, +2.48°, $[\alpha]_D^{20}=61.7$; 13 minutes, +2.46°; 21 minutes, +2.88°; 24 minutes, +2.22°; 1½ hours, +0.83°; 2½ hours, +0.4°; 4½ hours, +0.31°; 26 hours, +0.25° (minimum); 46 hours, +0.32°; 70 hours, +0.39°; 114 hours, +0.40°; from which we calculated the additional values for $[\alpha]_D^{20}$: 13 minutes, +61.4°; 21 minutes, +56.9°; 24 minutes, +55.4°; 90 minutes, +20.7°; 150 minutes, +10.0°; 270 minutes, +7.74°; 1,560 minutes, +6.24°; 46 hours, +7.99°; 70 hours, +9.74°; 114 hours, +10.0°.

tone shown in Curve III. Curve II shows the change in specific rotation of the oxidation product from glucose after bromine oxidation in which the excess bromine was removed by olive oil. The rotations were calculated as given in the experimental portion of the paper. After the first 30 minutes, Curve III drops more rapidly than Curve II, while for the first 30 minutes Curve II drops slightly more rapidly than Curve III. This is due to the fact that the sample shown in Curve II is buffered with sodium acetate and acetic acid, while Nef's solution shown in Curve III is not buffered; initially the sample shown in Curve II is slightly more acid than Nef's solution on account of the acetic acid in the buffer, but as the lactone shown in Curve III hydrolyzes it becomes more acid than the solution shown in Curve II. Curve IV shows the mutarotation of a buffered solution of gluconic acid. The specific rotation starts with a negative value and changes at approximately the same rate as the rotations of the oxidation product and the delta lactone. After 400 minutes the value reaches approximately that shown in Curves II and III. In the latter portion of all the curves a gradual rise in rotation occurs, as one would expect, since the final products are the same.

The marked similarity of the mutarotation of the oxidation product (Curve II) to the mutarotation of the delta lactone (Curve III), together with the dissimilarity to the mutarotation of gluconic acid (Curve IV) indicates that the rapidly mutarotating substance is the delta or 1,5 gluconic lactone. If we interpret the fact that lactone formation precedes the formation of gluconic acid to indicate that one ring form of the sugar is oxidized directly to the lactone, we can not say whether or not the particular form of the sugar which is oxidized is the predominating form in solution. Nevertheless it is of interest that the delta or 1,5 lactone is found in solution after the oxidation of a solution containing normal glucose which supposedly contains a 1,5 ring.

Since the lactone appears in solution immediately after the oxidation, if the sugar ring is broken it must be closed again within a few minutes. This might be accomplished by means of an intermediate compound which has the property of condensing rapidly to form the lactone. But regardless of the exact mechanism whereby the lactone is formed, its appearance prior to that of gluconic acid gives a new conception for the oxidation of the aldose sugars in slightly acid solution.

III. BROMINE OXIDATION OF VARIOUS SUGARS

Inasmuch as the specific rotations of the lactones of the aldose sugars differ in value, it is reasonable to assume that the corresponding sugars on bromine oxidation should show similar variations in the values of their specific rotations. Our experimental results indicate that such is the fact. In addition, our observations have shown that in each case a series of changes occurs which indicates that the delta lactones are the first products which can be detected and that the acids which appear subsequently are secondary products resulting from the hydrolysis of the lactones. Some of the lactones which are indicated by these observations are not known at present, but will undoubtedly be prepared in the future.

The experimental method was essentially that outlined for glucose. In each case the same quantities by weight of the reagents and sugar (anhydrous) were used. The rotations were read in a 1dm tube and calculated to the specific rotations which are based upon the weight of sugar. The temperatures were maintained as near 20° as possible, but the large amount of heat liberated in the reactions caused some variations. Further experiments are in progress wherein the conditions are more rigidly controlled, the results of which will be treated in subsequent publications.

1. OXIDATION OF *d*-GALACTOSE

The changes in rotation which occur on the oxidation of galactose (fig. 3, Curve I) resemble those found for glucose in that the specific

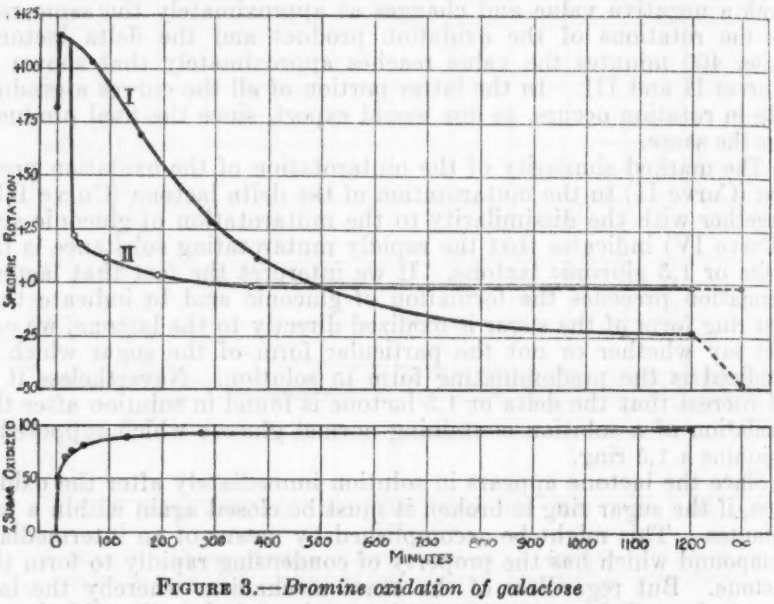


FIGURE 3.—*Bromine oxidation of galactose*

I, changes in the specific rotation of the sugar during the oxidation.

II, changes in the specific rotation of a portion of the solution after interrupting the oxidation by removing the bromine with sodium thiosulphate.

rotation increases initially, then decreases rather rapidly for several hours. Subsequently the rotation decreases very slowly to a constant negative value which corresponds to the equilibrium condition between the acid and the lactones. Obviously the highly dextro rotatory oxidation product is not galactonic acid which exhibits a negative specific rotation [10] ($[\alpha]_D^{20} = -10.6$). The rotation of the oxidation product decreases on standing while the rotation of galactonic acid first increases, reaching a maximum in about two hours, then slowly decreases.[11] The initial rise in the rotation of the solution after bromine oxidation indicates that the delta galactonic lactone (presumably formed) is more dextro rotatory than the sugar. The

[10] Ruff and Franz, Ber., vol. 35, p. 948, 1902.
[11] Levene and Simms, J. Biol. Chem., vol. 65, p. 41, 1925.

rapid decrease in rotation is caused by the hydrolysis of this lactone which proceeds until a quasi equilibrium with the free acid is established. As the gamma lactone continues to form, the negative rotation of the solution increases because the specific rotation[12] of the gamma lactone ($[\alpha]_D^{20} = -77$) is even more negative.

2. OXIDATION OF *l*-ARABINOSE

The changes in rotation which occur on the oxidation of arabinose (fig. 4, Curve I), are very similar to those found for galactose. The marked similarity might be expected from the closely related structures. The delta arabonic lactone which at present is not known also

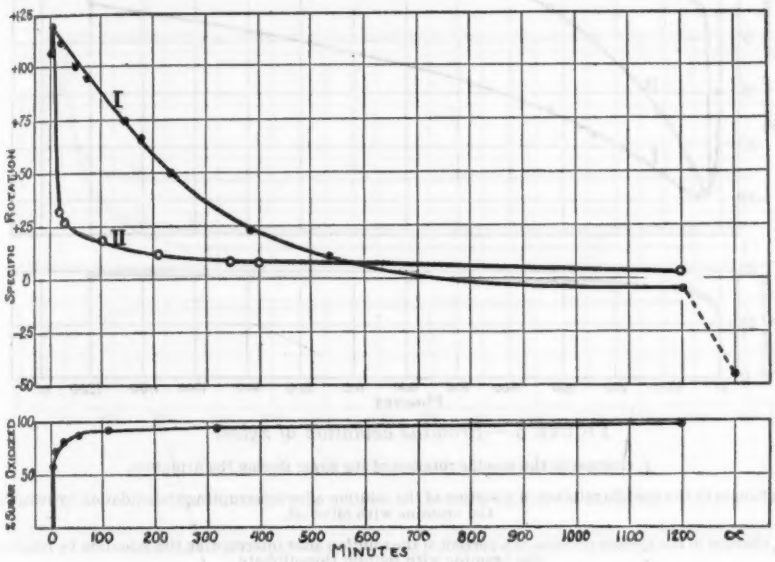


FIGURE 4.—*Bromine oxidation of arabinose*

I, changes in the specific rotation of the sugar during the oxidation.

II, changes in the specific rotation of a portion of the solution after interrupting the oxidation by removing the bromine with sodium thiosulphate.

appears to be more dextro rotatory than the free sugar. The specific rotations of *l*-arabonic acid and its gamma lactone are reported as $[\alpha]_D^{20} = -9$ [13] and $[\alpha]_D^{20} = -73$,[14] respectively. A comparison of the specific rotation of the free acid with specific rotation of the sugar during the oxidation shows that the acid is not the initial oxidation product.

3. OXIDATION OF *d*-XYLOSE

Although the changes in rotation which occur on the oxidation of *d*-xylose, as shown by the specific rotation curves (fig. 5) appear to be quite different from those previously given, they indicate that similar phenomena are taking place. The curves appear different because the first product, presumably the delta lactone, has a negative rotation,

[12] Nef, Ann., vol. 403, p. 276, 1914.
[13] Allen and Tollens, Ann., vol. 260, p. 312, 1890.
[14] Fischer and Piloty, Ber., vol. 24, p. 4219, 1891.

causing the rotation to decrease initially. As this strongly negatively rotating lactone is hydrolyzed to the free acid the negative specific rotation decreases to zero. After becoming positive it increases as the dextro rotating gamma lactone [15] is formed. The delta xylonic lactone is not known at present, but these results indicate it has a strongly negative specific rotation.

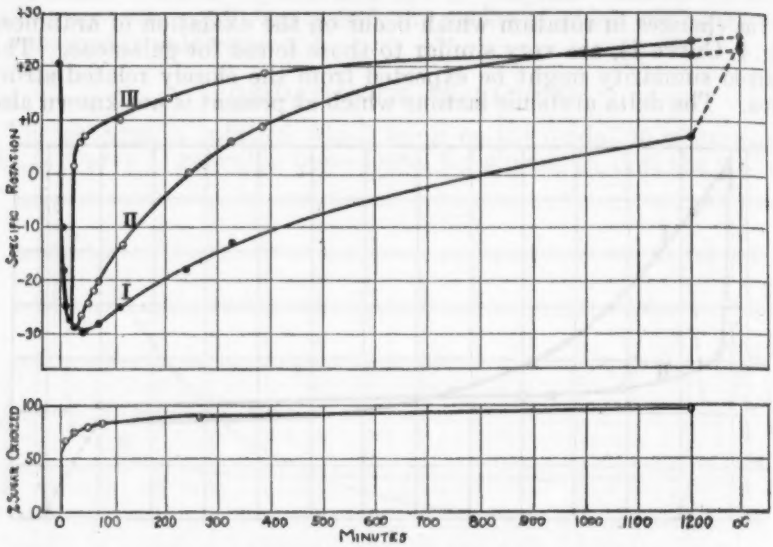


FIGURE 5.—*Bromine oxidation of xylose*

I, changes in the specific rotation of the sugar during the oxidation.

II, changes in the specific rotation of a portion of the solution after interrupting the oxidation by removing the bromine with olive oil.

III, changes in the specific rotation of a portion of the solution after interrupting the oxidation by removing the bromine with sodium thiosulphate.

4. OXIDATION OF LACTOSE

The oxidation of lactose is of particular interest because the fourth carbon in this sugar is substituted and the corresponding monobasic acid can not form a gamma lactone. The changes in rotation (fig. 6, Curve I) show that only a single lactone is formed. The oxidation curve for lactose differs from the other sugars in that it does not give the final slow change in rotation characteristic of the gamma lactones. The type of specific rotation curve obtained with this sugar is additional evidence supporting the hypothesis that the delta lactones are formed prior to the sugar acids in the course of the oxidation of the normal aldose sugars by bromine water. The lactone of lactobionic acid is not known in the crystalline state. The initial rise in rotation shown in Curve I indicates that the rotation of this lactone is more dextro than the rotation of lactose.

[15] According to Clowes and Tollens, $[\alpha]_D^{20} = +74.4$. Ann., vol. 310, p. 175, 1900.

IV. EXPERIMENTAL DETAILS

The oxidation of glucose was conducted in the following manner: 27½ g of α-*d*-glucose monohydrate (25 g of anhydrous sugar), 37.5 g of crystalline sodium acetate and 2.5 ml of glacial acetic acid were dissolved in sufficient water to give 244 ml. After 18 hours the rotation was measured at 20° with a Bates saccharimeter; the solution was then cooled to +8° and 8.75 ml of bromine were added, making the total volume of the solution 250 ml. The solution was shaken vigorously until the bromine was completely dissolved, which required one or two minutes. The temperature rose rapidly to 20° where it was maintained by occasional immersion of the flask in an

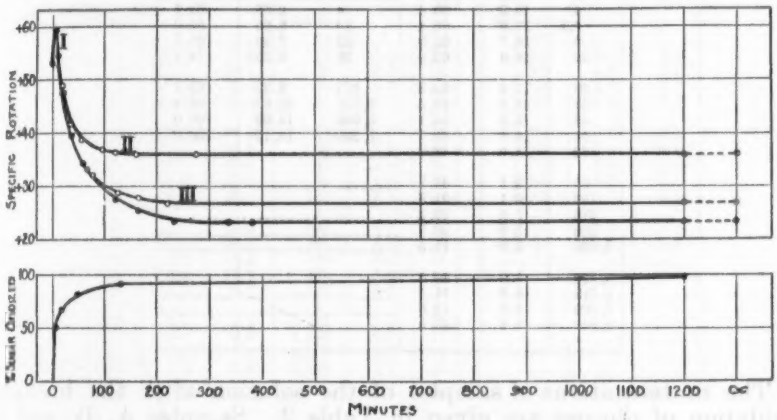


FIGURE 6.—*Bromine oxidation of lactose*

I, changes in the specific rotation of the sugar during the oxidation.

II and III, changes in the specific rotations obtained from portions of the solution after interrupting the oxidation at different times by removing the bromine with olive oil.

ice bath. Since it was desired to obtain readings as soon as possible the solution could not be kept in a thermostat, and, consequently, it was not possible to control the temperature very closely during the early stages of the reaction. A portion of the oxidation solution was transferred to a 1 dm polariscope tube and the rotation read every few minutes. The readings are given under "Rotation of the solution," Table 1. Simultaneously, samples of the oxidation solution were pipetted into small glass-stoppered flasks which contained 25 ml of a 10 per cent potassium iodide solution, and the free bromine was determined by titration with sodium thiosulphate. The amount of bromine used in the oxidation of the sugar was obtained by the difference in the titration of a blank which contained the same quantity of bromine, but did not contain any glucose, and the titration of the sample. The results are expressed in Table 1 as ml of N/10 bromine used per ml of the sugar solution.

TABLE 1.—*Bromine oxidation of glucose at 20° C.*

1 dm tube, international sugar degrees
25 g glucose ($\alpha=\beta$)
37.5 g sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$)
2.5 ml glacial acetic acid
Water to make a total volume of 250 ml after the addition of 8.75 ml bromine

Rotation of the solution			Bromine determination		
ΔT	°S.	$[\alpha]_D^{20}$	ΔT	Bromine used per ml sugar solution	Sugar oxidized
Minutes			*Minutes*	*ml N/10 solution*	*Per cent*
0	15.0	+52.4			
4	19.0	66.4	4	5.85	52.7
6.5	19.0	66.4	14	6.65	59.9
9	18.7	65.3	32	7.30	65.7
22	18.0	62.9	56	8.25	74.3
28	17.4	60.8	172	9.30	83.7
38	15.9	55.5	1,375	10.60	95.4
46	15.5	54.1	5,940	11.00	99.0
54	14.8	51.7	7,200	11.10	100.0
62	14.0	48.9			
85	12.5	43.7			
159	9.1	31.8			
216	7.5	26.2			
300	5.8	20.3			
1,360	3.3	11.5			
4,320	3.0	10.5			
5,713	3.3	11.5			
7,200	3.6	12.6			
8,640	3.8	13.3			

The mutarotations of samples of the solution after the bromine oxidation of glucose are given in Table 2. Samples A, B, and C were taken at different times, and the oxidation stopped by removing the excess bromine by shaking with olive oil. In this manner the excess bromine is removed very quickly without changing the acidity of the solution. A small amount of decolorizing carbon was added and the mixtures were filtered through dry filter papers directly into polariscope tubes. The polariscopic readings for each sample are recorded under "°S." The "per cent of glucose" oxidized was obtained from the amount of bromine used as given in Table 1. The unoxidized glucose is the difference between the amount originally added and the amount oxidized by the bromine water. The rotation of the unoxidized glucose is computed upon the assumption that the specific rotation of the unoxidized glucose remains constant and equal to +52.4°.[16] The "lactone formed" per ml of solution is calculated from the bromine used, by multiplying the values for the ml of *N*/10 bromine used (see Table 1) by the factor 0.0089. The rotation of the "lactone formed" is equal to the difference between the rotation of the solution and the rotation of the unoxidized glucose, and the specific rotation of the "lactone" is equal to this difference expressed in circular degrees divided by the weight of lactone per ml of solution.

[16] The calculations were made upon the assumption that the mutarotation of the solution was due solely to the oxidation product. Probably certain forms of the sugar are more easily oxidized than others. Hence one form may be preferentially oxidized and the equilibrium of the various forms of the sugar may be displaced. This equilibrium disturbance would cause the rotation of the unoxidized sugar to change as the sugar approached equilibrium. The preliminary results indicate that any error which may arise from an equilibrium disturbance under the specific experimental conditions is small, but the subject is being investigated further.

TABLE 2.—*Mutarotation of samples after bromine oxidation of glucose*

(The excess bromine was removed with olive oil)

Sample A			Sample B			Sample C		
Lactone formed=0.0521 g per ml Unoxidized glucose=0.0473 g per ml			Lactone formed=0.0592 g per ml Unoxidized glucose=0.0401 g per ml			Lactone formed=0.0943 g per ml Unoxidized glucose=0.0046 g per ml		
ΔT	°S.	Calculated $[\alpha]_D$ lactone	ΔT	°S.	Calculated $[\alpha]_D$ lactone	ΔT	°S.	Calculated $[\alpha]_D$ lactone
Minutes			*Minutes*			*Minutes*		
4			14			1,375		
8	18.2	73.3	19	18.0	69.8	1,380	3.3	9.5
10	17.7	70.1	26	16.7	62.2	1,393	3.3	9.5
12	17.3	67.4	30	15.9	57.4	1,465	3.2	9.2
16	16.2	60.1	41	14.5	49.3	1,525	3.2	9.2
25	15.0	52.0	48	13.9	45.8	1,585	3.0	8.5
29	14.5	48.8	65	12.9	40.0	4,285	3.4	10.0
40	13.5	42.0	81	12.0	34.6	5,715	3.8	11.5
47	13.2	40.1	98	11.5	31.8	7,165	3.9	11.8
64	12.5	35.5	161	9.8	21.8	8,605	4.1	12.5
79	11.7	30.1	213	9.1	17.7	25 days	5.0	15.8
97	11.1	26.1	274	8.6	14.9	40 days	5.0	15.8
160	9.9	18.2	306	8.4	13.7			
315	8.8	10.9	372	8.2	12.5			
370	8.5	8.8	1,360	8.1	11.8			
1,360	8.4	8.3	1,585	8.0	11.3			
1,585	8.3	7.5	4,320	8.1	11.8			
4,320	8.3	7.5	7,200	8.2	12.5			
7,200	8.5	8.8	8,640	8.2	12.5			

TABLE 3.—*Comparison of optical rotations of the oxidation product (sample A) with Nef's lactone* [1]

Oxidation product		Nef's less stable gluconic lactone	
Time	$[\alpha]_D^{20}$	Time	$[\alpha]_D^{20}$
Minutes		*Minutes*	
6	+73.3		
8	+70.1		
10	+67.4	12	+61.7
14	+60.1	13	+61.4
23	+52.0	21	+56.9
27	+48.8	24	+55.4
95	+26.1	90	+20.7
158	+18.2	150	+10.0
1,585	+7.5	1,560	+6.24

[1] See footnote 9, p. 330.

TABLE 4.—*Mutarotation of gluconic acid at 20° C.*[1]

1 dm tube, International sugar degrees.
0.0139 mole, sodium gluconate or 13.9 ml *N*/1 solution.
0.0137 mole, sodium acetate or 1.86 g $NaC_2H_3O_2 \cdot 3H_2O$.
0.0184 mole, acetic acid = 1.02 ml glacial acetic acid.
0.0278 mole, hydrobromic acid = 4.06 ml 6.85 *N*/1 solution.
Sufficient water to make a total volume of 25 ml.

ΔT	°S	$[\alpha]_D^{20}$[2]	ΔT	°S	$[\alpha]_D^{20}$
Minutes			*Minutes*		
4.5	−1.8	−6.29	87	+1.3	+4.55
5.5	−1.7	−5.94	100	+1.3	+4.55
6.5	−1.6	−5.60	113	+1.6	+5.60
9	−1.6	−5.60	129	+1.7	+5.94
12	−1.2	−4.20	170	+1.8	+6.29
15	−1.0	−3.50	210	+1.95	+6.82
19	−.7	−2.45	286	+2.0	+6.99
26	−.5	−1.75	1,455	+2.4	+8.39
30	−.2	−.70	1,825	+2.6	+9.09
36	+.05	+.17	6,195	+3.7	+12.94
44	+.4	+1.40	7,575	+3.85	+13.46
54	+.6	+2.10	8,160	+4.0	+13.99
64	+.85	+2.97	13,920	+4.6	+16.09
75	+1.1	+3.85	----------	+5.0	+17.49

[1] Equivalent concentrations to those in sample C, Table 2.
[2] Calculated upon the weight of the lactone.

WASHINGTON, January 11, 1932.

FLUCTUATIONS OF THE RATE OF EMISSION OF α-PARTICLES FOR WEAK SOURCES AND LARGE SOLID ANGLES

By L. F. Curtiss

ABSTRACT

An investigation of the fluctuations in the rate of emission of α-particles from very weak polonium sources (of the order of 3×10^{-12} curie/mm^2) for solid angles approximately equal to 4π has been made, using automatic registration and a special double Geiger point counter. The object was to try to detect the large deviations for weak preparations reported by Pokrowski (Z.S. für Phys., vol. 58, p. 706, 1929; and vol. 59, p. 427, 1930). The total number of particles counted for two different sources was about 306,700 recorded in 14 different sets of observations at average rates of from 300 to 45 per minute, representing practically the total rate of emission from each source. The values of Q^2 for each set of observations were computed from the expression

$$Q^2 = \frac{\overset{x}{\underset{0}{\Sigma}} l_x x^2}{L} - m$$

where l_x is the number of equal intervals, each containing x α-particles, m is the the average number per interval and L is the number of α-particles observed. This divergence coefficient, which for a random distribution equals unity, varied between 0.828 and 1.110 for the 14 different sets. The average value of Q^2 obtained, however, is 1.004 which indicates that under these conditions there is no appreciable deviation from a purely random distribution.

CONTENTS

	Page
I. Introduction	339
II. Description of apparatus	340
III. Experimental results	344

I. INTRODUCTION

Investigations of the accuracy with which the distribution of the rate of emission of α-particles conforms to that required by the law of probability have quite generally failed to show any perceptible deviation from the probability distribution. Renewed interest in this problem has resulted in several recent studies intended to detect small deviations from random distributions. In addition to observations on sources acted upon by some external stimulus, such as X rays or γ rays, considerable attention has been paid to radioactive preparations under normal conditions in an effort to discover anomalous effects. Attempts of this kind have been encouraged, in part at least, by the development of improved methods of automatic registration which might be expected to reveal small discrepancies which formerly were missed as the result of the subjective errors possible in the scintillation method of studying the problem, which, in the early investigations, was the only method available.

The investigation here described deals only with preparations in the absence of external stimulus. Furthermore it is not concerned with those deviations from random distributions such as have been reported by Kutzner and others,[1] using fairly concentrated preparations and which may be explained as the result of aggregate recoil. The present work was undertaken to test, by a different method from those previously employed, the suggestion of Pokrowski[2] that very weak sources might show deviations from a probability distribution. The experiments which he performed to test this idea were done with zinc sulphide screens artificially "contaminated" with a small amount of radioactive material (about 10^{-12} gm/mm^2). He reports decided deviations from a random distribution of such nature that very short intervals between appearances of particles occur much more frequently than is demanded by probability. On the other hand, two subsequent studies have been described, one by Herszfinkiel and Dobrowolska[3] and the other by Feather,[4] both using methods quite similar to those described by Pokrowski, but failing to confirm his results.

Since the experiments just mentioned were all done by the scintillation method it was thought possible that the disagreement which they exhibit could be referred in some way to the difficulties of making such observations and the possiblity for errors, particularly where a large number of scintillations are counted by a single observer. This consideration led the writer to undertake a few experiments, described in this paper, to test the weak source hypothesis of Pokrowski by a method using entirely automatic registration.

II. DESCRIPTION OF APPARATUS

In making a test of this hypothesis it is necessary to make certain of including as large a solid angle as possible since Pokrowski postulates that this anomalous behavior of weak preparations is the result of two somewhat independent phases of the condition which exists in a weak preparation. He assumes that the reaction of a disintegrating atom may increase the probability of one of its neighbors disintegrating even to the extent of causing it to disintegrate simultaneously; and, since there is little likelihood of both particles thus ejected travelling in the same direction, one of the particles would fail to be counted if, as usual, particles emitted within a small solid angle are observed. In his experiments he imbedded the radioactive material in the zinc sulphide screen to avoid this difficulty. If anything of this kind occurs it can best be detected by observations which include practically all the particles emitted by a preparation so that, if peculiar spatial distributions are present, these can also affect the results.

The apparatus used in the present experiments was designed to count as nearly as is practicable all the particles emitted by the source in all directions. A special double Geiger point counter was used for this purpose. It is shown diagrammatically in Figure 1. The two counting chambers are separated by a thin aluminum foil, F, of about 5 mm stopping power. The polonium source, P, is formed by allow-

[1] Kutzner, W., Z. S. für Phys., vol. 21, p. 281, 1924. Curtiss, L. F., B. S. Jour. Research, vol. 4 (RP 166), p. 595, 1930.
[2] Pokrowski, G. I., Z. S. für Phys., vol. 58, p. 706, 1929; vol. 59, p. 427, 1930.
[3] Herszfinkiel, H., and Dobrowolska, H., Z. S. für Phys., vol. 62, p. 432, 1930.
[4] Feather, N., Phys. Rev., vol. 35, p. 705, 1930.

ing a small drop of a very dilute solution of polonium to evaporate on the foil. This solution was prepared by depositing a little polonium from a RaD solution on a bit of silver foil and then dissolving the foil in nitric acid. This solution was then diluted until sources of the desired strength could be obtained from it. The aluminum foil on which the source is deposited is mounted on a metal slide, *H*, and completely covers the circular opening therein. Thin sheet metal shutters, not shown, were provided which could be inserted in the slots, *S*, *S*, one on each side of the foil and close to it. These shutters were useful in determining the proper voltage for the counting chambers and in making certain that the chambers were working properly. Since the chamber walls of both counters were in metallic contact, any difference in operating voltages was taken care of by a biasing potential applied to one needle. *G*, *G* are guard rings connected to earth. In operation, the whole counter was inclosed in an air-tight copper box filled with dry air at atmospheric pressure.

To make certain that as large a proportion as possible of the total number of particles emitted by the source would be counted, specially sharpened steel points were used. The actual point had such a

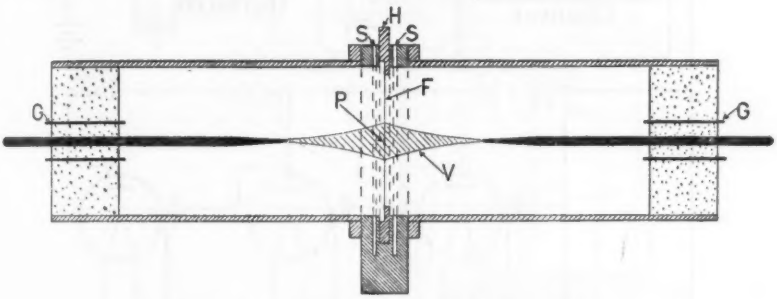


FIGURE 1.—*Diagram of double point counter*

curvature that the active volume, *V*, as indicated by the shaded region in Figure 1, was a cone which at its base was five or six times the diameter of the source itself. The diameter of the source was about 2 mm. Under these circumstances it can be seen that only particles traveling in the plane of the foil will fail to be counted since those which diverge even a very small amount from this plane must traverse a sufficient section of the active volume to produce a response in the counting chamber since a fraction of a millimeter of the path of the α-particle falling within the active volume will do this. Careful tests were made to insure that the active volume fulfilled the requirements set above. Although it is difficult to estimate what fraction of the particles emitted near the plane of the foil will not be counted, it seems probable that this can not amount to more than 5 per cent.

Since it was found simpler to use a single amplifier in connection with the registration of the impulses of the counter, the two points were connected together and all impulses from both points were fed into one recording system. This method of making the record will adequately serve to reveal the deviations in question, if they exist; for, although by this arrangement the simultaneous emission of the particles in opposite directions can not be observed, the failure to register these will increase the error of the observations and conse-

quently will increase the divergence from a probability distribution. In a like manner if, as Powkrowski assumes, there is a great preponderance of very short intervals some of these particles will fail to be recorded if these intervals are less than the resolving power of the recording system. On the other hand, this use of a single amplifier eliminates all disturbing effects of recoil atoms, should any have sufficient energy to be counted, since the effect of the recoil atom will be included simultaneously with that of the α-particle which produced it. As a matter of fact, very little if any effect of recoil atoms could be detected. This was tested by connecting one counting chamber with the amplifier and introducing thin mica screens just in front of the aluminum foil separating the two counters. If any recoil radiation

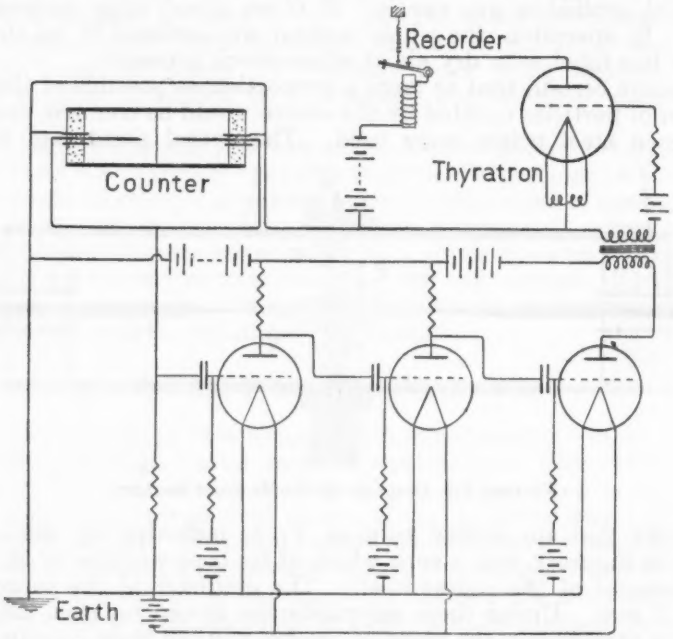


FIGURE 2.—*Vacuum tube amplifier and connections*

were present at all it would be very easily absorbed so that the introduction of a screen of a few millimeters stopping power should produce a decrease in the rate of counting. No such effect was observed.

The connection of the counter with the three-stage resistance-capacity coupled amplifier is shown in Figure 2. The time constants of the various stages were chosen to give satisfactory results at fairly high counting rates in order to make certain that the "resolving power" of the arrangement was limited only by that of the mechanical recorder used. In determining the best values for these constants it was found that the final choice could best be made by actual trial in the amplifier in agreement with the experience of Fränz.[5] In fact, the chief difference between this amplifier and that used by Franz is the use of a blocking condenser in the input stage. In order to elimi-

[5] Fränz, H., Z. S. für Phys., vol. 63, p. 373, 1930.

nate difficulties which are common with mechanical relays, a thyratron, connected as shown, was used to amplify the output sufficiently to give sharp powerful action in the mechanical recorder.

The mechanical recorder was of special construction shown in Figure 3, designed to reduce the inertia of moving parts as much as possible and to be suitable for use with a thyratron. A thin iron armature, *A*, is pivoted so that it may be drawn downward by the electromagnet, *E*. The spring, *S*, which holds the armature up against the support for the contact buttons is mounted in such a way that its tension can be adjusted. A thin phosphor bronze spring, *P*, carrying an intermediate contact button is mounted as shown, in electrical contact with the support carrying the fixed contact. This spring and intermediate contact is required because provision must be made to

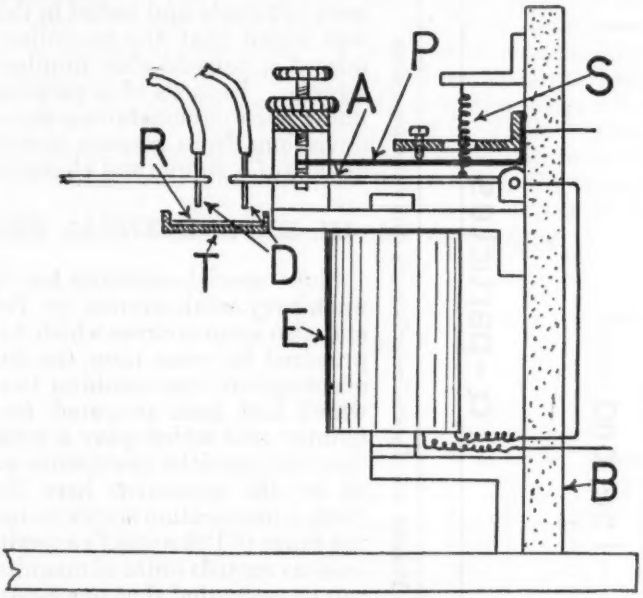


FIGURE 3.—*Diagram of mechanical recorder*

interrupt the plate circuit of the thyratron to reset it for the next signal. However, the break can not be made at the instant the armature starts downward, as would occur if the fixed contact alone were used, since then the action would be too feeble. By means of the intermediate contact the plate circuit can be interrupted at different points on the down stroke of the armature depending on the position of the adjusting screw which regulates the position of *P*. The wires protruding through the hard rubber base, *B*, are connected, one to the plate of the thyratron, and the other to the positive terminal of the thyratron plate battery, as shown in Figure 2. The outer end of the armature, *A*, carries a short metal tube, *D*, about 0.5 mm diameter. This serves as a dotting pen and is connected with a stationary ink reservoir by a fine rubber tube. When the armature is pulled down the pen makes a dot on the paper ribbon, *R*, moving at right angles to the plane of the figure in the trough shown in cross section at *T*. Another similar dotting pen records time signals.

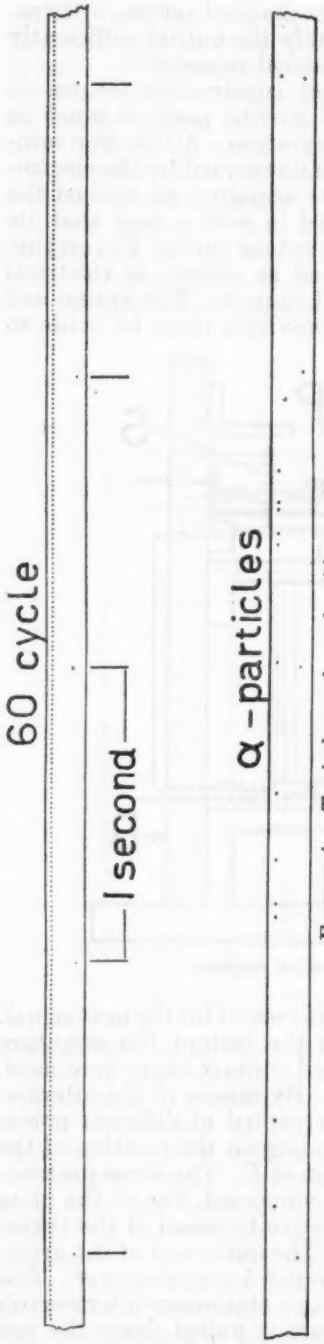


FIGURE 4.—*Typical records made with recording system*

This device is capable of recording signals at the rate of more than 100 per second. An example of a record is shown in Figure 4. The upper record is made from the 60 cycle a. c. supply and the lower is part of a record where α-particles are being recorded at an average rate of about 300 per minute. The time dots, in this case at one second intervals, also appear on each record. It was found convenient to use records made from the 60 cycle supply in adjusting the recorder. When careful adjustments were not made and tested in this way it was found that the recording system missed a considerable number of the signals. Records of α-particles made under such circumstances showed wide deviations from random distributions, always of a subnormal character.

III. EXPERIMENTAL RESULTS

Since special emphasis has been put upon very weak sources by Pokrowski and also upon sources which have been prepared for some time, the final set of observations were made on two sources which had been prepared for several months and which gave a total of less than 100 particles per minute as recorded by the apparatus here described. Such a preparation seems to fall within the range of Pokrowski's experiments, at least as regards order of magnitude. It can be estimated that one α-particle per second in a solid angle of 4π from a polonium source equals approximately 2×10^{-11} curies.[6] Since the area of both faces of the source is about 8 mm^2 this gives for the sources used approximately 2.5×10^{-12} curie/mm^2 as compared with the concentration given by Pokrowski (Z. S. für Phys., vol. 58, p. 706,1929) of "about 10^{-12} gm/mm^2." Of the records made, the longest contained about 40,000 particles and the shortest 7,000. The longer records were made at an average rate of about 100 per minute so that no set of observations required more than seven hours. Therefore, no correction was made for the natural rate of decay of the polonium source since for this period it is negligible.

[6] Gregoire, C. R., vol. 193, p. 42, 1931.

The resolving power of the apparatus was estimated at 1/100 second. This was deduced from its performance, as shown in Figure 4, in counting 60 cycle pulses. For this resolution the accuracy for an average counting rate at 1 per second is 99 per cent. For a counting rate of 5 per second, it is 95 per cent. Another factor which, of course, must be considered in comparing the results with those required by probability is the number of particles included in a record. For this reason those records which have fewer particles may be expected to show greater variations than the longer records. However, as will be seen, even the shortest records give reasonable agreement with probability distributions it is assumed that all records contain a sufficient number of particles to justify a comparison with a random distribution.

The comparison of the results with those to be expected according to probability was made by computing the Lexis divergence coefficient, Q^2, as explained elsewhere.[7] For a normal distribution $Q^2=1$. For a supernormal distribution, such as Pokrowski found, where the number of intervals differing considerably from the mean interval are in excess, $Q^2>1$. The results are tabulated in Table 1 where Σl_x is the total number of equal intervals for which α particles were counted; x is number of particles in an interval, hence $\Sigma x l_x$ is the total number of particles counted. $\Sigma x^2 l_x$ and m, the average number of particles per interval, are used in the expression for obtaining Q^2

$$Q^2=\frac{\sum_0^x x^2 l_x}{\Sigma x l_x}-m$$

TABLE 1

Date	Σl_x	$\Sigma x l_x$	$\Sigma x^2 l_x$	m	Interval	Q^2
1931					*Second*	
October 8	4,926	26,653	166,263	5.411	1	0.828
	7,160	39,307	254,389	5.490	1	.982
October 9	3,634	16,242	89,070	4.470	1	1.014
October 15	2,050	11,972	83,210	5.840	5	1.110
October 16	2,234	12,213	79,623	5.467	5	1.052
	1,977	8,155	42,061	4.125	5	1.033
October 17	1,473	7,281	42,631	4.943	5	.912
October 20	4,219	22,902	145,850	5.428	5	.940
October 21	4,236	22,873	145,949	5.400	5	.982
October 22	3,755	25,306	195,294	6.739	5	.978
October 28	4,241	34,863	324,689	8.221	5	1.092
October 29	3,399	26,423	234,419	7.774	5	1.098
October 30	3,851	31,981	309,969	8.348	5	1.038
October 31	2,243	20,524	208,400	9.150	5	1.004

A test of whether a set of Q^2 shows a genuine departure from the values to be expected is given by Bortkiewicz.[8] This test consists of comparing the mean value of the Q^2 with mean error of the Q^2 defined by

$$M(1/\nu\sum_1^\nu Q_i^2)=1/\nu\sqrt{\sum_1^\nu M^2(Q_i^2)}$$

[7] Curtiss, L. F., B. S. Jour. Research, vol. 4 (RP166), p. 595, 1930.
[8] v. Bortkiewicz, L., Die Radioaktive Strahhlung als Gegenstand wahrscheinlichkeitstheoretischer Untersuchungen, Julius Springer, Berlin, 1913.

where ν equals the number of sets of observations from which the values of Q_i^2 ($i=1, 2 \ldots \nu$) where determined and $M^2(Q_i^2)=\frac{2m_j+1}{L_j}$ where L_j = total number of particles counted for that set of observations. Table 2 contains quantities required to determine the mean error for the observations recorded in Table 1.

TABLE 2

Q^2	m	L	$M^2(Q_j^2)$
0.828	5.411	26,653	0.000406
.982	5.490	39,307	.000302
1.014	4.470	16,242	.000612
1.110	5.840	11,972	.001060
1.052	5.467	12,213	.000985
1.033	4.125	8,155	.001134
.912	4.943	7,281	.001495
.940	5.428	22,902	.000531
.982	5.400	22,873	.000516
.978	6.739	25,306	.000572
1.092	8.221	34,863	.000500
1.098	7.774	26,423	.000627
1.038	8.348	31,981	.000553
1.004	9.150	20,524	.000940
$\sum_1^{\nu} (Q_j^2)=14.063$			$\sum_1^{\nu} M^2(Q_j^2)=.010233$

Inserting the numerical values in the expression for the mean error

$$1/\nu\sqrt{\sum_1^{\nu} M^2(Q_i^2)}=1/14\sqrt{0.010233}=0.00721$$

The average value of $Q^2=\frac{14.063}{14}=1.004$ so that the deviation of the average from the expected value of unity is 0.004. This is approximately one-half the mean error (0.00721) just computed. We can conclude, therefore, that the variations exhibited by the Q^2 fall well within those permitted theoretically and the deviations of the Q^2 from unity are to be regarded as accidental and not systematic.

In view of the foregoing there seems to be little room to doubt that laws of probability are accurately followed even in the low concentrations of active material which are dealt with here. It thus seems logical to conclude that probability laws apply over an enormous range of concentrations, roughly, from 10^{-3} to 10^{-12} gm/mm^2, since the accuracy with which concentrated preparations conform to an exponential rate of decay verifies the application of probability laws in their case. Consequently, in view of the fact that these laws hold for concentrations varying by a factor of about 1,000 million, leaves little room to doubt that they would apply for any concentration which we are able to measure or observe.

The writer wishes to acknowledge the help of Miss C. L. Torrey and L. L. Stockman and B. W. Brown in making and counting records and in the computation of the numerical results.

WASHINGTON, January 18, 1932.

GASES OBTAINED FROM COMMERCIAL FELDSPARS HEATED IN VACUO

By G. R. Shelton and H. H. Holscher [1]

ABSTRACT

This paper constitutes a preliminary report of an investigation to determine quantitatively the gases obtained by heating a feldspar in vacuo. Nineteen samples representative of the ground commercial material, such as is used in the ceramic industry, were tested. At 1,000° C. the gases consisted, by weight, of 32 to 96 per cent water vapor, 0 to 59 per cent acid gases, and 0 to 36 per cent unabsorbed gases. Calculated to volume relations a unit of feldspar when heated to 1,000° C. would evolve (extremes for the 19 samples) 16 to 140 volumes of water vapor and 0 to 15 volumes of acid gases (assumed to be CO_2) measured at 1,000° C.

CONTENTS

	Page
I. Introduction	347
II. Materials	348
III. Method	348
IV. Apparatus	348
V. Procedure	349
VI. Experimental data	351
1. Results at 1,000° C	351
2. Loss on ignition as basis for calculating kaolinite	352
3. Effects of temperature	353
4. Flint and mica	355
5. Minor gas constituents	355
6. Volume relations of gases	355
VII. Summary and conclusions	356
VIII. Acknowledgments	356

I. INTRODUCTION

This paper constitutes a preliminary report on an investigation which has for its purpose the determination of the nature and quantity of gases obtained from a number of typical ground commercial feldspar when heated in a vacuum.

There is a possibility that gases derived from such feldspars or the minerals normally associated with commercial feldspars during the firing process may affect some of the physical properties of bodies and glazes in which feldspar is one of the principal ingredients; for example, the minute gas bubbles in dental porcelain of high feldspar content might be expected to originate from the gas evolved from the feldspar or associated minerals.

Various investigators have analyzed the gases obtained from lavas and rocks when heated in vacuo. Shepherd [2] found water vapor to be the most important constituent of gases yielded by these materials. Chamberlain [3] lists over 100 analyses of gases extracted from rocks and minerals and gives a complete review of the subject up to the time of his publication.

[1] Cooperative fellow, Bureau of Standards and Engineering Experiment Station of Ohio State University.
[2] E. S. Shepherd, The Analysis of Gases Obtained from Volcanoes and from Rocks, J. Geol., vol. 33, p. 289, 1925. E. S. Shepherd and H. E. Merwin, J. Geol., vol. 35, p. 97, 1927.
[3] R. T. Chamberlain, Gases in Rocks, Carnegie Institute of Washington, Publication No. 106, 1908.

II. MATERIALS

The 19 feldspar samples investigated were portions of the same ground commercial samples previously studied at the Bureau of Standards, on which fairly comprehensive data have been published.[4] It must be noted that the feldspars are not pure minerals, but that they contain other minerals, such as quartz, hornblende, biotite, muscovite, and calcite in varying quantities as indicated by Insley.

III. METHOD

A discussion of gravimetric methods for the determination of gases at low pressures is given by Jordan, Swindells, and Eckman.[5] As a result of their work on the efficiency of gas absorbents at rather low pressures solid reagents were found to be most suitable. Consequently, in the present investigation phosphours pentoxide was used for the absorption of water vapor and ascarite for acid gases. Provision was made for the oxidation of hydrogen and carbon monoxide by passing the gases over heated copper oxide. The water vapor and carbon dioxide formed were then absorbed by phosphorus pentoxide and ascarite, respectively.

IV. APPARATUS

The apparatus used in this investigation was developed at the Bureau of Standards for the analysis of gases obtained from metals by fusion in vacuo.[6] Its essential parts consisted of a method for circulating and absorbing the gases, which is completely described by Vacher and Jordan, and of a furnace for heating the specimen in vacuo.

The furnace was of the usual platinum-resistance type, having an auxiliary heater.[7] The vacuum chamber (fig. 1) consisted of a fused silica tube, 1 inch inside diameter and 12 inches long, closed at the bottom. The open end of this tube, projecting from the furnace, was fitted with a water-jacketed brass tube, the joint between the two tubes being sealed with picein cement. The brass tube was joined to the glass system of the apparatus, picein cement being used to seal this joint also. Additional cooling of the end of the tube projecting from the furnace was obtained by means of a cooling coil attached to the container with zinc cement. This cement was made by moistening with sodium silicate solution a 1 to 1 mixture of powdered and granular (20 to 30 mesh) metallic zinc. The mixture was dried first at room temperature and finally at about 150° C.

Furnace temperatures were determined by means of a platinum to platinum-rhodium thermocouple, permanently mounted inside the furnace, so that it touched the outside of the vacuum chamber. Frequent comparisons of this couple with a standard couple were made.

---

[4] H. Insley, J. Am. Cer. Soc., vol. 10 (9), p. 651, 1927. R. F. Geller and A. S. Creamer, J Am. Cir. Soc., vol. 14 (1), p. 30, 1931.

[5] L. Jordan and F. E. Swindells, Cases in Metals: I. BS. Sci. Paper No. 457, 1922. L. Gordan and J. R. Eckman, Gases in Metals, II. B. S. Sci. Paper No. 514, 1925; III. B. S. Sci. Paper No. 563, 1927.

[6] H. C. Vacher and Louis Jordan, The Determination of Oxygen and Nitrogen in Irons and Steels by the Vacuum-Fusion Method, B. S. Jour. Research, vol. 7 (2), p. 375, August, 1931.

[7] 25 feet of 25-gage platinum wire were wound, 12 turns to the inch, on the inner refractory tube 2 inches in diameter. Coaxial with this tube was one 4 inches in diameter wound with nichrome ribbon, which constituted the auxiliary heater. The space between the tubes was filled with Al_2O_3, and the larger tube was insulated with diatomaceous earth. Asbestos boards at top and bottom of the metal cylinder held the tubes in place.

V. PROCEDURE

Before each test was made on a feldspar sample, the vacuum chamber was heated to 1,000° C. and allowed to cool to room temperature, with the pressure in the entire system reduced to 1 mm or less.

Approximately 10 g[8] of feldspar, previously dried at 105° to 110° C., were placed in a weighed fused silica test tube and then put into the vacuum chamber, which in turn was lowered into the furnace. The brass tube was sealed to the container and the glass welded to the analytical train as already explained. The ascarite and phosphorus pentoxide tubes were filled,[9] connected to the apparatus and evacuated to about 2 mm pressure. The evacuated tubes were then removed and weighed, the lubricant having been removed from the tips of the side arms with ether. Trials indicated that constant weight of the tubes was obtained after repeated lubricating and cleaning of the side arms. The weighed evacuated tubes were again connected to the apparatus, and the glass system evacuated to 2 mm or less. Before proceeding further, tests were made for leaks.[10] Pressure was read on the McLeod gauge, which was then shut off from the system and the ascarite tube was closed. The stopcocks were adjusted so that the gases were forced to circulate through the phosphorus pentoxide tube. The furnace was then heated

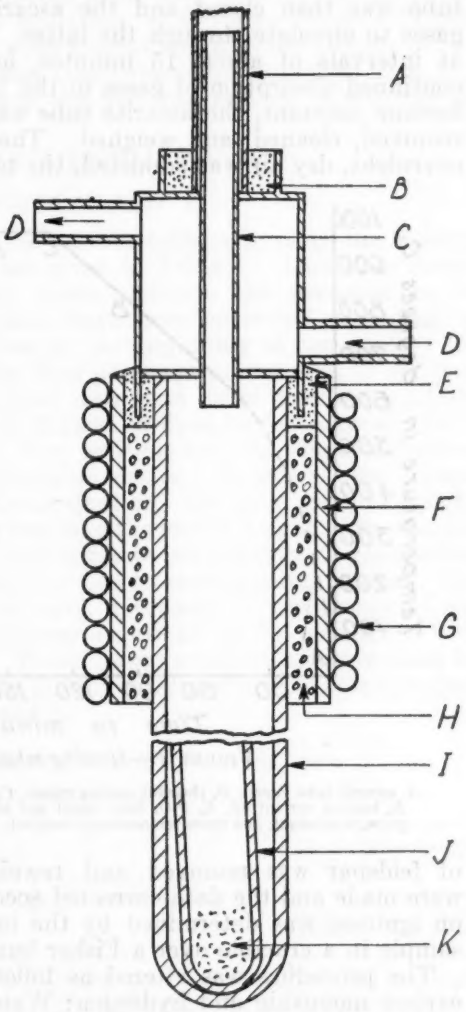


FIGURE 1.—*Sample container*

A, pyrex tubing leading to glass system; *B*, picein cement; *C*, water-jacketed brass tube; *D*, water inlet and outlet; *E*, picein cement; *F*, brass collar with soldered coil *G*; *H*, zinc cement; *I*, fused silica vacuum chamber; *J*, fused silica test tube with feldspar sample K.

[8] Preliminary tests indicated that sufficient gas could be obtained from a 10 g sample of feldspar to give checks within the limits of error of the method employed.

[9] Ascarite will lose water slowly if kept for a long time in an evacuated system. Although not done in this study, it is advisable to pack small amounts of P_2O_5 on each side of the ascarite.

[10] A high-frequency violet ray machine was used in testing for leaks. The terminals were held on opposite sides of the tube or stopcock being tested. The path of the spark between the terminals always passed through the leak, making its location a simple matter.

to 1,000° C. according to the heating schedule shown in Figure 2. This temperature was held constant for 30 minutes, and the heating current turned off. During this period and for 30 minutes after the heating current was turned off, the gases from the feldspar were circulated through the phosphorus pentoxide tube.[11] The tube was then closed and the ascarite tube opened, causing the gases to circulate through the latter. Pressure readings were made at intervals of about 15 minutes, lower pressures indicating the continued absorption of gases in the tube. After the pressure had become constant, the ascarite tube was also closed, and both tubes removed, cleaned, and weighed. The furnace was allowed to cool overnight, dry air was admitted, the test tube containing the sample

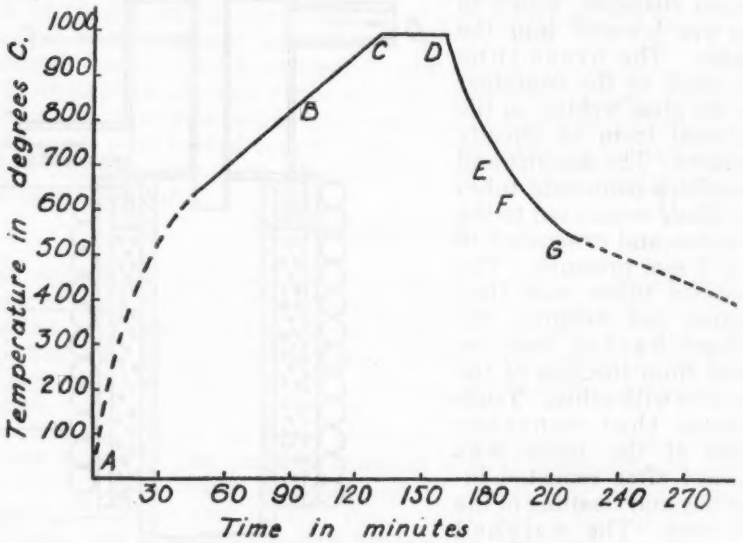


FIGURE 2.—*Heating schedule of feldspars*

A, ascarite tube closed; *B*, rheostat setting raised; *C*, temperature 1,000° held for 30 minutes; *D*, heating current off; *E*, P_2O_5 tube closed and ascarite tube opened; *F*, pressure read; *G*, pressure constant, and tubes removed and weighed.

of feldspar was removed and reweighed. Blank determinations were made and the data corrected accordingly. Total loss of weight on ignition was determined by the usual method of heating a 1 g sample in a crucible over a Fisher burner.

The procedure was altered as follows when tests were made for carbon monoxide and hydrogen: Water and acid gases were determined as explained above. The absorption tubes were again connected to the system, the adjoining part of which was then evacuated. The gases in the remainder of the system were passed through a U tube filled with copper oxide heated to 300° C. in order to oxidize hydrogen to water and carbon monoxide to carbon dioxide. Any water vapor formed would be absorbed in the P_2O_5 tube and carbon dioxide by the

[11] Tests indicated that this procedure was necessary to avoid condensation of water in the glass system connected with the furnace. If water were permitted to condense, a much longer time was required for its absorption by the P_2O_5.

ascarite. The circulation of gases was continued until pressure readings became constant. From the weighed amounts of CO_2 and H_2O thus obtained, the quantities of CO and H_2 originally present in the gases could be calculated. A correction was made for the gas inevitably lost when the absorption tubes were disconnected from the system and weighed, before oxidation of CO and H_2 was begun. Knowing the volume of the entire system and also the volume of the system adjoining the absorption tubes (between stopcocks 2, 3, and 5) it was possible to calculate the gas lost and its percentage of CO and H_2.

VI. EXPERIMENTAL DATA

1. RESULTS AT 1,000° C.

The results obtained from the various feldspars, using the heating schedule shown in Figure 2, are given in Table 1. Duplicate determinations, reported in many cases, indicate the precision to be expected. The anyalytical data have been corrected according to the blank determinations given at the beginning of the table. Inspection of this table indicates that good agreement was, in general, obtained between the analytical data and total loss on ignition. This indicates that the amount of gases evolved by feldspars at 1,000° C. in a vacuum is no greater than ignition loss, the slight difference probably being due to unavoidable errors. In every case except one (feldspar No. 12, first determination) the total gain in weight of the two absorption tubes is less than the loss in weight of the sample heated in the furnace. This may indicate the presence of gases other than those absorbed, or it may be due to experimental errors. The amount of the gaseous constituents, expressed as percentage of the total gas, varied as follows: Water vapor 32 to 96, acid gases 0 to 59, and other gases 0 to 36. Water vapor constituted more than 50 per cent of the absorbed gases obtained from every feldspar studied with the exception of Nos. 2 and 5.

TABLE 1.—*Gases evolved by 19 typical ground feldspars*

[Results of determinations at 1,000° C.]

Feldspar No.[1]	Gain in weight		Total gain in weight	Loss of sample	Difference[2]	Loss on ignition	Composition by weight of evolved gases		
	Ascarite tube	P_2O_5 tube					Acid gases	Water	Other gases
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Blank	0.002	0.016	0.018	0.026	0.008	----	----	----	----
1	.00	.19	.19	.23	.04	0.27	----	----	----
	.02	.21	.23	.24	.01	.27	----	----	----
Average	.01	.20	.21	.24	.03	.27	4	84	12
2	.20	.11	.31	.34	.03	.40	59	32	9
3	.11	.28	.39	.50	.11	.50	----	----	----
	.10	.37	.47	.56	.09	.53	----	----	----
	.09	.32	.41	.48	.07	.48	----	----	----
Average	.10	.32	.42	.51	.09	.50	20	62	18

[1] The sample numbers used are the same as those used by Geller and Creamer, Investigation of Feldspar and Its Effect in Pottery Bodies, J. Am. Cer. Soc., vol. 14, No. 1, January, 1931.

[2] Includes nonabsorbed gases and any material which may volatilize in the crucible, but condense before reaching the analytical train.

TABLE 1.—*Gases evolved by 19 typical ground feldspars*—Continued

[Results of determinations at 1,000° C.]

Feldspar No.	Gain in weight		Total gain in weight	Loss of sample	Difference	Loss on ignition	Composition by weight of evolved gases		
	Ascarite tube	P_2O_5 tube					Acid gases	Water	Other gases
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
4	0.21	0.39	0.60	0.71	0.11				
	.20	.45	.65	.70	.05	0.64			
Average	.20	.42	.62	.70	.08		29	60	11
5	.25	.20	.45	.46	.01	.50			
	.22	.19	.41	.50	.09	.57			
Average	.24	.20	.43	.48	.05	.54	49	41	10
6	.04	.31	.35	.42	.07	.48			
	.03	.33	.36	.48	.12	.51			
	.02	.35	.37	.45	.08	.46			
Average	.03	.33	.36	.45	.09	.48	7	73	20
7	.04	.34	.38	.46	.08	.46			
	.02	.40	.42	.47	.05	.47			
Average	.03	.37	.40	.47	.07	.47	6	79	15
8	.18	.23	.41			.64			
	.19	.25	.44	.70	.26	.69			
	.18	.29	.47	.71	.24	.65			
	.18	.28	.46	.72	.26	.65			
Average	.18	.26	.44	.71	.25	.66	26	38	36
9	.03	.19	.22	.26	.04	.33	12	73	15
10	.07	.33	.40	.42	.02	.47	16	79	5
11	.06	.18	.24	.24	.00	.25	25	75	0
12	.03	.12	.15	.13	−0.02	.17			
	.01	.14	.15	.17	.02	.20			
Average	.02	.13	.15	.15	.00	.19	13	87	0
13	.02	.20	.22	.29	.07	.30			
	.01	.22	.23	.28	.05	.30			
	.01	.20	.21	.26	.05	.26			
Average	.01	.21	.22	.28	.06	.29	4	75	21
14	.01	.26	.27	.30	.03	.28	3	87	10
15	.02	.19	.21	.23	.02	.24	9	82	9
16	.00	.24	.24	.27	.03	.31	0	89	11
17	.00	.94	.94	.98	.04	.95	0	96	4
	.02	1.02	1.04			1.03			
18	.08	.15	.23	.26	.03	.29	31	58	11
19	.01	.18	.19	.21	.02	.21	5	85	10

The presence of such minerals as muscovite, pyrite, and calcite in the commercial feldspars [12] may account for some of the variations noted in the analyses of gases obtained from them. For instance the high percentage of acid gases in feldspar No. 5 was undoubtedly due in part to carbon dioxide derived from calcite found in this sample by microscopic examination.

2. LOSS ON IGNITION BASIS FOR CALCULATING KAOLINITE

Since the gas obtained by heating a feldspar is a mixture and not pure water vapor, the loss on ignition of a feldspar should not be used in calculating its kaolinite content, except where approximate results

[12] See footnote 4, p. 348.

only are desired. Otherwise too high a percentage of kaolinite would be indicated.

3. EFFECTS OF TEMPERATURE

A study was made of the amounts of water vapor and acid gases obtained from feldspars when the temperature to which they are heated is gradually increased. A preliminary investigation was made to determine the loss on ignition of four feldspars, Nos. 1, 4, 15, and 19. Gram samples were heated at 105°, 200°, 300°, 400°, 500°, 600°, and 750° C. in a Hoskins muffle furnace. The temperature was held constant for a period of three days when the sample was removed, cooled in a dessicator, and weighed. The furnace temperature having been increased by 100° C., the sample was returned and allowed to

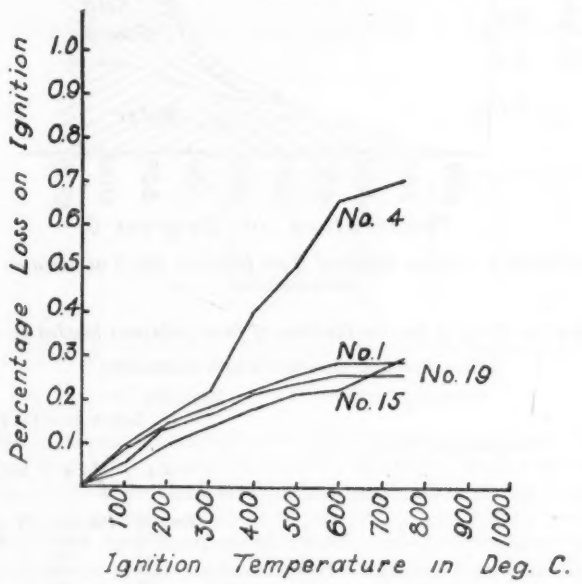


FIGURE 3.—*Rate of loss on ignition of four feldspars at various temperatures*

remain at the higher temperature for a second period of three days. The results are given in Table 2 and are also shown in the form of curves in Figure 3.

Feldspar No. 5 was selected for vacuum treatment at various temperatures, since in previous tests it was found to yield a large amount of acid gases. (See Table 1.) Following the procedure described in Section V, the sample was heated to 400° C. and then the increase in weight of the absorption tubes and the decrease in weight of the sample in the vacuum furnace were determined. The sample was returned to the furnace and a similar determination made at 500° C., the process being repeated at 100° intervals up to 1,000° C. The results are given in Table 3 and plotted as curves in Figure 4. Water vapor is the chief constituent of the gas obtained at 400° C., the quantity reaching a maximum between 800° and 900° C. The evolution of acid gases starts between 400° and 500° C., becomes most rapid at

about 700° C., and is practically completed at 800° C. Small amounts of gases other than water vapor and acid gases were indicated as low as 600° C. Since all the weight of experimental errors falls on the determination of these unabsorbed gases, the values obtained for them should not be overemphasized.

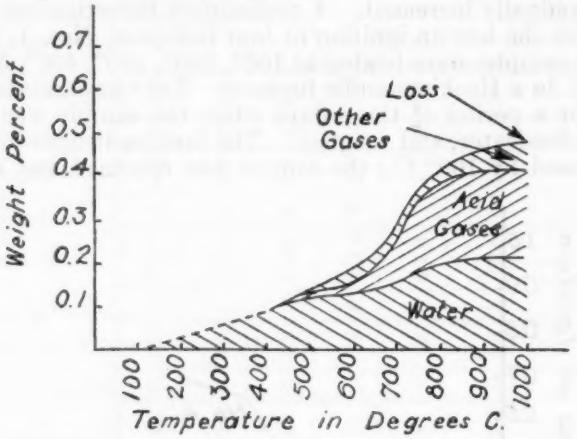


FIGURE 4.—*Gases obtained from feldspar No. 5 at various temperatures*

TABLE 2.—*Rate of loss on ignition of four feldspars headed in air*

(Time of heating: three days at each temperature)

Temperature (° C.)	Loss in weight of feldspar			
	No. 1	No. 4	No. 15	No. 19
	Per cent	*Per cent*	*Per cent*	*Per cent*
105	0.08	0.09	0.04	0.06
200	.14	.16	.09	.13
300	.18	.22	.13	.17
400	.22	.41	.18	.21
500	.25	.50	.21	.24
600	.28	.66	.22	.26
750	.28	.70	.29	.26
Loss between 105–750	.20	.61	.25	.20
Loss on ignition [1]	.27	.64	.24	.21

[1] Of sample dried at 105–110° C. Table 1.

TABLE 3.—*Gases evolved from feldspar 5 at various temperatures*

Temperature (° C.)	Acid gases	Water	Total	Loss of sample	Difference	Loss on ignition
	Per cent [1]	*Per cent* [1]	*Per cent* [1]	*Per cent* [1]	*Per cent* [1]	*Per cent* [1]
400	0.00	0.09	0.09	0.09	0.00	
500	.01	.12	.13	.12	−.01	
600	.02	.12	.14	.18	.04	
700	.10	.16	.26	.29	.03	
800	.20	.19	.39	.42	.03	
900	.21	.21	.42	.45	.03	
1,000	.20	.21	.41	.48	.07	0.50

[1] Accumulative per cent.

4. FLINT AND MICA

Flint and mica being the two most common impurities in commercial feldspar used in the ceramic industries, a determination of the gas obtained from each was made by using the same procedure employed in case of the feldspars. The flint was a commercially ground quartz sand, and the mica was also a ground commercial product. The mica was of coarser grain than the feldspar.

The results of these tests are given in Table 4. Water was the only gas obtained from the flint, but both water and acid gases were evolved by the mica. In analyzing gases obtained from feldspars the results would not be seriously affected by the acid gases derived from the small amounts (less than 4 per cent) of mica present.

TABLE 4.—*Results obtained when using copper oxide to determine CO and H_2 at 1,000° C.*

Sample No.	Acid gases	Water	CO	H_2	Total	Loss of sample	Difference	Loss on ignition
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
5	0.22	0.19	0.00	0	0.41	0.50	0.09	0.57
6	.01	.35	.00	0	.36	.45	.09	.46
8a	.18	.29	.12	0	.59	.71	.12	.65
8b	.18	.28	.08	0	.54	.72	.18	.65
13	.01	.20	.00	0	.21	.26	.05	.26
17	.02	1.02	.00	0	1.04	(1)	-------	1.03
Flint	.00	.09	.00	0	.09	.11	.02	.12
Mica	.20	4.11	.00	0	4.31	4.80	.49	4.80

[1] Sample dusted out of small container due to too rapid evacuation and therefore could not be weighed.

5. MINOR GAS CONSTITUENTS

Hydrogen was not detected and carbon monoxide was indicated in only one sample (No. 8 in Table 4). It is not to be supposed from the evidence available that the carbon monoxide came from the feldspar itself or that the presence of an inclusion which might be the source of this gas has been established. Refinements of the method will be required in order to determine such gases as hydrogen sulfide, sulfur dioxide and nitrogen, should they be present.

6. VOLUME RELATIONS OF GASES

The volume of gases obtained from unit volume of the feldspars was calculated from the gravimetric data. The calculations involved the assumption that water vapor acted as a perfect gas at a temperature above 400° C. and that the acid gases were composed entirely of carbon dioxide. The resulting values, necessarily approximate, are given in Table 5. The following are the extremes at 1,000° C. for the 19 feldspars: One milliliter would yield from 16 to 140 ml of water vapor and from 0 to 15 ml of acid gases (as CO_2) measured at 1,000° C.

TABLE 5.—*Volume of gases evolved at different temperatures from feldspar No. 8*

[Time of heating, one-half hour at each temperature; size of sample, 10 g; volume of gas, calculated at maximum temperature of each range]

Temperature range (°C.)	CO_2	CO	Water vapor
	ml	*ml*	*ml*
0–400	0	0	43
400–500	0	<1	21
500–600	1	<1	24
600–700	7		17
700–800	14	3	33
800–900	[1] 5		9
900–1,000			6
1,000–1,100		7	6
1,100–1,200		[2] 26	[2] 10
Total	27	37	171

[1] Evolution of CO_2 is complete at 900° C.
[2] Evolution of CO and H_2O continues at least up to 1,200° C.

VII. SUMMARY AND CONCLUSIONS

The amounts of water vapor and acid gases were determined in 19 samples of ground commercial feldspars when heated in vacuo at a series of temperatures increasing in steps of 100° from 400° to 1,000° C. The quantities of carbon monoxide and hydrogen were determined in some of these samples. A study also was made of the gases obtained on heating two of these feldspars from 400° to 1,200° C., in steps of 100° C.

Water vapor began to come off as soon as the samples were heated above the drying temperature; the maximum amount was obtained between 800° and 900° C. The evolution of acid gases started at about 500° C., the speed of evolution increasing rapidly between 600° and 900° C. No hydrogen and only small quantities of carbon monoxide were found.

At 1,000° C. the gases were found to consist by weight of 32 to 96 per cent water vapor, of 0 to 59 per cent acid gases, and of 0 to 36 per cent unabsorbed gases. Volume calculations indicated that 1 ml of feldspar would yield 16 to 40 ml of water vapor and 0 to 15 ml of acid gases (calculated as CO_2) measured at 1,000° C.

VIII. ACKNOWLEDGMENTS

The above investigation was carried out under a cooperative agreement between the Bureau of Standards and the Engineering Experiment Station of Ohio State University. Greatful acknowledgement is made to T. A. Klinefelter, L. Jordan, and H. C. Vacher, and also to Prof. A. S. Watts, who represented the Engineering Experiment Station, for advice and assistance.

WASHINGTON, June 8, 1931.

EXPERIMENTS ON THE EMISSION AND ABSORPTION OF RADIATION BY METALLIC SILVER

By F. L. Mohler

ABSTRACT

The emission spectrum of silver bombarded by electrons is characterized by a high intensity from the visible to 3,600 A, with a decrease to a very low value beyond 3,200 A.

The spectrum emitted by silver bombarded by 100-volt electrons in high vacuum is similar to the emission of a silver probe surface at a low positive potential in a cæsium discharge.

Probe emission spectra at different temperatures have been compared and a small effect found which may or may not be a pure temperature effect. The slope between 3,600 A and 3,200 A becomes slightly less with a shift toward longer wave length with increasing temperature.

The absorption of a silvered quartz plate has been measured at temperatures between 20° and 490° K. There is a large increase in absorption with increasing temperature limited to the range 3,350 to 2,950 A with a maximum effect at 3,100 A. The effect is a decrease in slope of the violet edge of the selective transmission band with increasing temperature.

The results are contrary to a theory proposed by Boeckner and the author. The observed change in emission is less and in absorption much greater than the predicted effect.

CONTENTS

		Page
I.	Introduction	357
II.	Radiation from silver bombarded by cathode rays in high vacuum	359
III.	Effect of temperature on silver emission	360
IV.	Effect of temperature on absorption	361
V.	Discussion	364

I. INTRODUCTION

In two recent papers [1] Boeckner and the author describe the continuous spectra emitted by metal surfaces bombarded by low-speed electrons. For most metals the radiation is a nearly equal energy spectrum of comparable intensity, but silver and copper show relatively intense characteristic emission bands. The silver band begins near 3,200 A, rises to a maximum near 3,600 A, and drops gradually with increasing wave length. The copper emission increases in the red. The abrupt increase comes at the points where the absorption and reflection of the metals suddenly increase. Thus, internal reflection and absorption tend to diminish the observed emission, and in paper No. 371 we have applied a correction for internal reflection by dividing observed intensities by $1-R$, where R is the reflection coefficient for normal incidence. The use of this reflection correction may be open to question, but for want of anything better I have

[1] Mohler and Boeckner, B. S. Jour. Research, vol. 6 (RP297), p. 673, 1931; and vol. 7 (RP371), p. 751, 1931. The second paper will subsequently be referred to as paper No. 371.

continued to use it. Figure 1 is taken from paper No. 371, and it shows the emission intensity distribution and the absorption curves for silver and copper. The edge of the silver band was shown to be exactly the form of the Fermi Sommerfeld distribution in energy for conduction electrons with an assumed temperature of 370° C., which is a reasonable value for the probe temperature under operating conditions.

This agreement suggested the theory that the emission process involves the ionization of a sharply defined underlying level with the consequent radiation transition of one of the conduction electrons into the ionized shell. This is identical with the process of characteristic X-ray emission, and Houston [2] has shown that the width of soft X-ray lines (*Be K* α in particular) corresponds closely to the predicted range of energy of the conduction electrons. Nevertheless, the theory as applied to the visible and near ultra-violet emission of silver is in certain aspects radical and extreme. The Fermi Sommerfeld distribution of energy is derived from an approximation which takes no

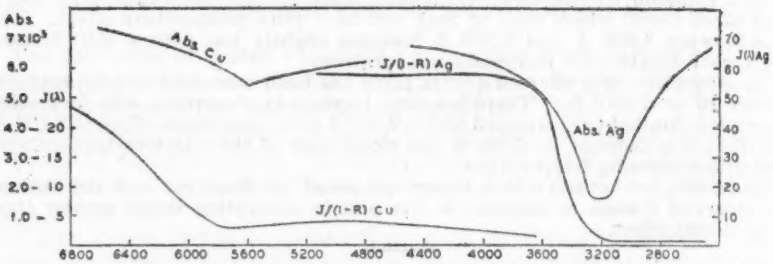


FIGURE 1.—*Intensity distribution of silver and copper radiation corrected for internal reflection, from paper No. 371*

Absorption coefficients of copper and silver in cm⁻¹.

account of atomic fields in a metal, and Houston's analysis of X-ray line shapes shows that the distribution is better represented by a theory of Bloch [3] which treats the electrons as moving in atomic fields which are greatly perturbed by close packing of the atoms. On this view an underlying level, 3.56 volts below the top of the continuum of conduction electrons, can not be sharply defined as was assumed to explain the silver emission.

In paper No. 371 it was suggested that the branch of the absorption curve extending toward shorter wave lengths came from absorption from the underlying level. If the level is appreciably broadened, then the violet edge of the emission band and the red edge of the absorption band will overlap, so this interpretation is not consistent with Bloch's theory.

The subject seemed to call for critical examination of the earlier work and further experiments to look for a temperature variation of the emission and absorption spectra of metallic silver. This paper reports three entirely separate experiments carried out for this purpose.

[2] Houston, Phys. Rev., vol. 38, p. 1797, 1931.
[3] F. Bloch, Phys. Zeits, vol. 32, p. 881, 1931.

II. RADIATION FROM SILVER BOMBARDED BY CATHODE RAYS IN HIGH VACUUM

Measurements of the silver emission have been made by observing the radiation emitted by a small probe surface at a positive potential in a cæsium vapor discharge. The cæsium discharge has the advantage that the radiation intensity of the vapor is very small, but the probe surface becomes cæsiated, and it may be questioned whether the radiation from the probe is characteristic of pure silver.

The technique of studying radiation of metals bombarded by electrons in high vacuum is being developed by L. S. Taylor, and will be described in detail later. To study silver radiation, I have used an oxide-coated platinum strip cathode about 1 mm from the anode,

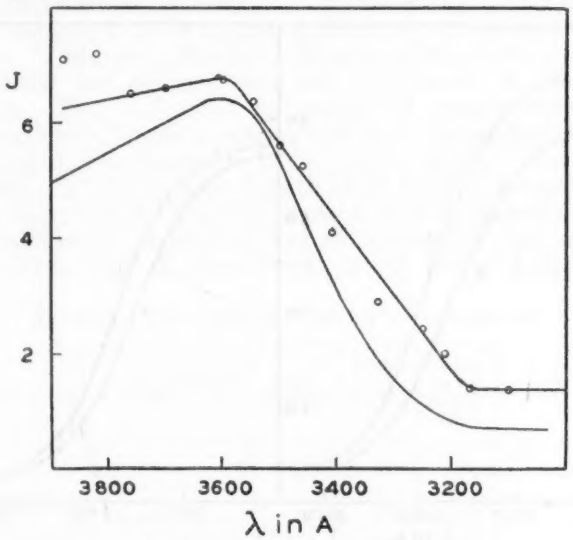


FIGURE 2.—*Emission of silver*

Upper curve with 100-volt electrons in vacuum; lower curve with 7-volt electrons in a cæsium discharge

which was a disk of silver 1 cm in diameter. The silver surface was viewed almost tangentially and the spectrum of the emitted radiation compared with a tungsten strip lamp. It was impossible to avoid discoloration of the silver by material distilled or sputtered from the cathode, and the silver radiation is doubtless more or less masked by impurities. Figure 2 shows the intensity distribution in vacuum at 100 volts and for comparison the silver radiation observed in a cæsium discharge at 7 volts. The vacuum intensity measurement is taken from a four and one-half hour exposure with a current of 16 ma. With this current the anode is maintained at a barely visible red heat, certainly less than 600° C. and probably above 550° C. This datum will be referred to later. Other spectrograms gave curves qualitatively like the one shown, though the shapes were never identical and the surface was always conspicuously contaminated. The important fact is that the short wave length edge of the emission band falls in the same wave length range (3,200 to 3,600 A) in vacuum as in cæsium

vapor. In paper No. 371 we include inaccurate measurements of silver radiation from a probe in a helium discharge which support the conclusion that cæsium does not modify the silver radiation.

III. EFFECT OF TEMPERATURE ON SILVER EMISSION

The radiation from a probe surface in a cæsium discharge has been used in these experiments with the arrangement of electrodes shown in paper No. 371 (fig. 1) except that the probe electrode was much heavier. A rod 1 cm in diameter was turned down to 3 mm at the end and all except this end surface insulated with glass. The rod was supported in a side tube of nearly the same diameter and the temperature of the side tube was controlled by a separate electric heater and measured by an external thermometer. The probe was

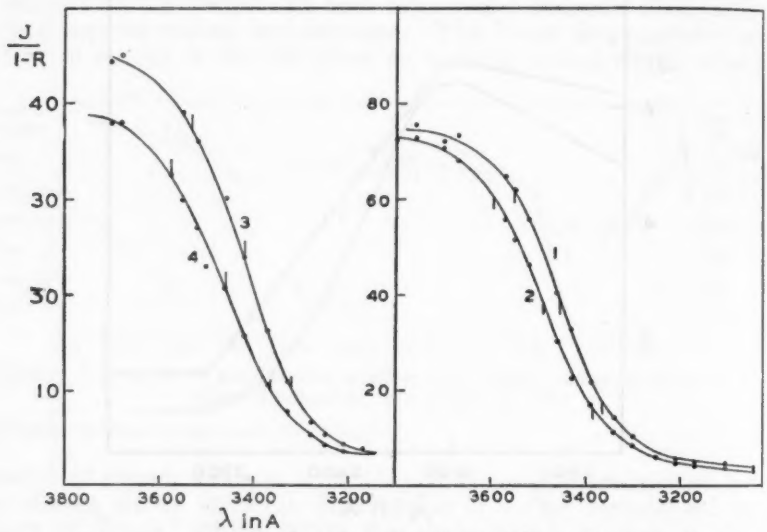


FIGURE 3.—*Intensity of silver radiation at different temperatures*

1 and 2 from successive exposures at 200° and 390° C.; 3 and 4 from exposures at 210° and 400° C. Points V_0, V_1, V_2 as defined in the text are indicated on each curve

designed to secure maximum thermal conductivity and it is probable that the temperature change of the exposed surface was about the same as that measured by the thermometer while the actual temperature was somewhat higher (estimated at 50° higher in Table 1) because of heating by electron bombardment.

The procedure was to compare exposures at a low temperature and at 200° to 300° above this temperature with conditions otherwise kept as constant as possible. However, there was evidence of some uncontrolled factor, probably surface contamination of the silver which caused the intensity to vary. Positive ion bombardment of the probe reduced the variation, but in general at higher temperatures the intensity and the intensity ratio J (3,700)/J (3,100) were lower. The temperature variation of the optical constants of silver described in the following section does not explain the difference.

Figure 3 shows two pairs of curves of $J(\lambda)/1-R$ as a function of λ. The temperature change was in each case about 200° C. Four such

pairs of curves and the two curves of Figure 2 have been analyzed in accord with the theory given in paper No. 371. $J=(J(\lambda)-J(3,100))/(1-R)$ plotted on a voltage scale (the scale is unimportant for this small range) is approximately of the form of a Fermi Sommerfeld distribution of energy [4] so we can write:

$$J=c/(\exp x+1) \qquad x=e\ (V-V_0)/kT \tag{1}$$

c is taken as $J(3,700)-J(3,100)$, V is the coordinate and V_0 the coordinate of the point where $J=c/2$. Values V_1 and V_2 of V have been determined for the points where $x=\pm 1.5$ $J=0.182\ c$ and $J=0.82\ c$. Then if the underlying assumptions are correct,

$$T=11{,}600\ (V_1-V_2)/3 \tag{2}$$

Table 1 summarizes the results. The estimated probe temperature is given in column 2 while column 3 gives the temperature computed from V_1-V_2. Column 4 gives the mid-point of the curve in Angstroms. The computed temperature does not correspond to the measured temperature. The difference in computed temperatures between two observations of a pair is always less than the temperature change and the computed temperature is, in general, greater than the actual temperature. A shift in wave length of 30 or 40 A toward the red at the higher temperature is shown in each pair of measurements; but, from the method of measuring and computing curves, comparisons between different sets of observations are of doubtful significance.

TABLE 1.—*The change in emission with temperature*

Figure and curve No.	Silver temperature	T °K. from equation (2)	Wave length of mid-point
	°K.		
Fig. 3, 1	473	735	3,455
Fig. 3, 2	663	810	3,490
	473	735	3,480
	673	810	3,510
	493	810	3,475
	793	890	3,505
Fig. 3, 3	483	850	3,420
Fig. 3, 4	673	850	3,460
Fig. 2, 1	600 (?)	640	3,465
Fig. 2, 2	820	890	3,470

IV. EFFECT OF TEMPERATURE ON ABSORPTION

There have been several papers on the temperature variations in the optical properties of silver; all of them qualitative observations showing a shift in the reflection and absorption minimum toward longer wave length and an increase in absorption with increasing temperature.[5] The following measurements of absorption were made

[4] Darrow, Phys. Rev. Supplement (Review of Modern Physics), vol. 1, p. 90, 1929.

[5] de Selincourt, The Effect of Temperature on the Anomalous Reflection of Silver, Proc. Roy. Soc., vol. 107, p. 247, 1925.
Rayleigh, The Ultra-violet Transmission Band of Silver as Affected by Temperature, Proc. Roy. Soc., vol. 128, p. 131, 1930.
McLennan, Smith, and Wilhelm, The Effect of Low Temperature on the Ultra-violet Transmission Band of Silver, Phil. Mag. vol. 12, p. 833, 1931.

using the usual methods of densitometry to compute the absorption from spectrograms of the transmitted light.

The source of light was a hydrogen discharge tube photographed end on with a Hilger E_2 quartz spectrograph. Two kinds of silver films were used; silver chemically deposited on a quartz plate, and silver evaporated in high vacuum onto the walls of a quartz bulb. The second method was tried in the hope that higher temperatures could be used without injuring the silver when it was in a vacuum, but no significant improvement or difference was seen. Both types of deposit rapidly deteriorate above 220° C. Measurements above room temperature were obtained by placing the plate or bulb in a small tube furnace and measuring the change in transmission with changing temperature. For the low temperature measurements liquid air or hydrogen was contained in a transparent quartz Dewar flask and the silvered disk immersed in the liquid. There was a large loss of light by scattering in passing through the flask and boiling liquid and measurements were made of the intensity change with and without the disk in the path of light.

Liquid hydrogen rapidly becomes clouded with solid air particles unless some precautions are taken. The hydrogen was forced by compressed hydrogen from the container into the quartz flask through a filter. With the mouth of the quartz flask stopped with cotton to reduce air circulation, the liquid remained clear for many minutes.

In the usual notation the transmission of a metal film of thickness x is expressed by the equation

$$J = J_0 \exp(-4\pi nk\, x/\lambda)$$
$$\log J_0 - \log J = (4\pi nk\, x/\lambda) \log e = a$$

Here J is the transmitted intensity corrected for loss of light by reflection. As the reflection is not known at the temperatures used we have omitted the correction, but the error introduced is small in the range where the temperature change is large. Between 3,050 and 3,250 it is less than 0.04 in $\log J - \log J_0$. Thus the observed change, 0.78 for the extreme range of temperature must measure predominantly a change in nk with temperature.

Several silver films, both evaporated and chemically deposited, were studied between 30° C. and 145° C. and the change in a was found to be nearly proprotional to a. Thus at 3,100 A the values of a were 0.96, 1.67, and 2.13 and the values of the change in a, divided by a at 30°, were 0.161, 0.165, and 0.160. This is consistent with the conclusion that the reflection correction is negligible.

Figure 4 gives measurements on a single sample at room temperature, 220° C. and −253° C. Deviations of measurements in liquid hydrogen from the mean curve for wave lengths greater than 3,400 A and less than 2,900 A are probably accidental. All other measurements indicate that there is no temperature effect outside of the range 2,900 to 3,350 A. Within this range the effect is large, giving a sixfold change in intensity at the maximum. The change is nearly proportional to the temperature difference. Thus between −253 and 30° C. the maximum change is 0.00178 per degree and between 40° C. and 220° C. it is 0.00156 per degree. A film of different thickness gave 0.00139 per degree between −180° C. and 145° C. which corresponds to 0.00152 per degree for equal thickness.

As the change is nearly proportional to the temperature one can apply a small correction to the curve at −253° C. to derive the form of the absorption curve at absolute zero, but the difference (0. 04 at the maximum) is scarcely appreciable.

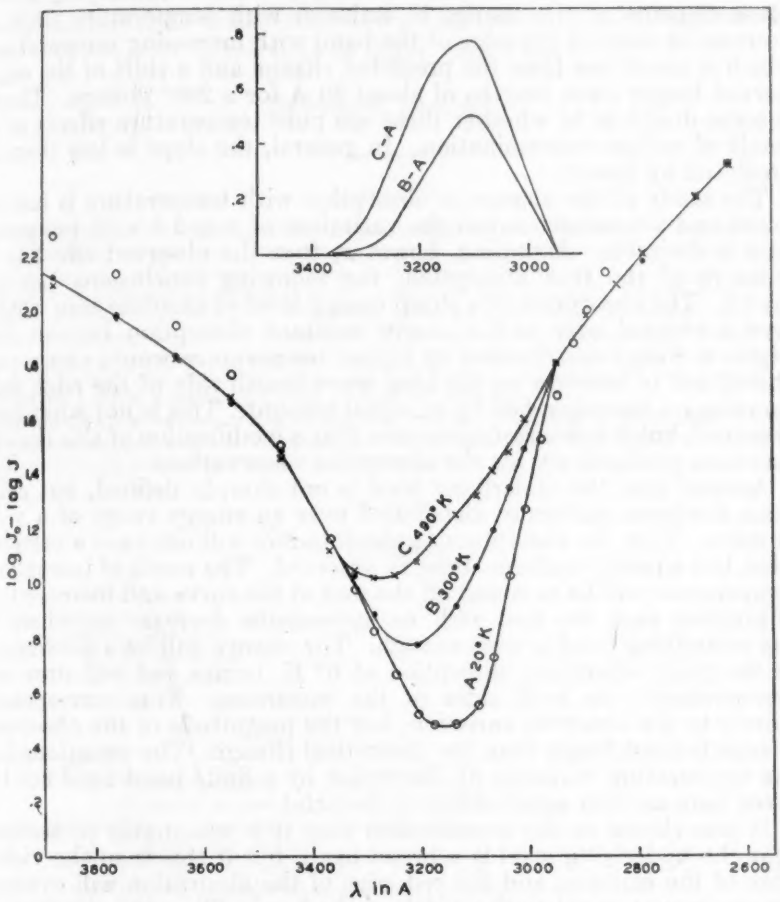


FIGURE 4.—*Absorption of a silver film at liquid hydrogen temperature, room temperature, and 220° C.*

Inset, the change in absorption, the difference between the lower curve and the other curves.

In published work interest has centered on the shift in the minimum of the absorption curve. The curves of Figure 4 give the following values for the minimum:

20° K., 3,155 A; 300° K., 3,220 A; 490° K., 3,275 A

In Figure 4 we include a plot of the temperature change as a function of wave length. Other measurements gave similar curves except that the two curves were not coincident at the short wave length side so this feature of the curves may be accidental.

V. DISCUSSION

The results do not support the theory proposed in paper No. 371 that the selective emission results from the transition of electrons from a Fermi distribution into a sharply defined underlying level. Measurements of the change in emission with temperature show a decrease in slope of the edge of the band with increasing temperature which is much less than the predicted change and a shift of the edge toward longer wave lengths of about 30 A for a 200° change. There is some doubt as to whether these are pure temperature effects or a result of surface contamination. In general, the slope is less than is predicted by theory.

The study of the change in absorption with temperature is inadequate and a measurement of the variations of n and k with temperature is desirable. Assuming, however, that the observed effect is a measure of the true absorption, the following conclusions can be drawn. The absorption of a sharp energy level at absolute zero would give a vertical edge and a nearly constant absorption beyond the edge. A Fermi distribution at higher temperature would cause the absorption to increase on the long wave length side of the edge and decrease on the other side by an equal amount. This is not what was observed, but it is interesting to note that a modification of this theory accounts qualitatively for the absorption observations.

Assume that the underlying level is not sharply defined, but contains electrons uniformly distributed over an energy range of a volt or more. Then the absorption at absolute zero will not have a vertical edge, but a nearly uniform slope, as observed. The result of increasing temperature will be to round off the foot of the curve and increase the absorption near the foot with no appreciable decrease anywhere if the underlying level is wide enough. The change will be a maximum at the point where the absorption at 0° K. begins and will drop off symmetrically on both sides of the maximum. This corresponds closely to the observed variation, but the magnitude of the observed change is much larger than the theoretical change. The equations for the temperature variation of absorption by a finite band need not be given here as their applicability is doubtful.

It was shown in the introduction that it is reasonable to assume that the underlying level is a broad band, but if this is so the violet edge of the emission and the red edge of the absorption will overlap by an amount equal to the width of the band. Thus the simple pictures of the absorption and emission processes that I have used are clearly inadequate. A theory such as one of Kronig [6] which accounts for absorption by transitions of electrons from a continuum of normal states, but with sharp selection principles governing the transitions can remove the apparent contradictions involved in pure energy considerations.

I am indebted to F. G. Brickwedde and J. W. Cook of the low temperature laboratory for their cooperation in the low temperature experiments and to C. Boeckner for many helpful suggestions.

WASHINGTON, January 4, 1932.

[6] Kronig, Proc. Roy. Soc., vol. 124, p. 409, 1929.

ACCELERATED WEATHERING TESTS OF SOLDERED AND TINNED SHEET COPPER

By Peter R. Kosting[1]

ABSTRACT

The pitting and furrowing of tinned and soldered sheet copper, which sometimes happen when weathered, were duplicated in the laboratory by exposing the copper to a humid atmosphere, rich in SO_2 and CO_2 at 50° C. or over. The progress of corrosion was followed by means of weight losses, tensile and bend tests. Extensive pitting and furrowing occurred only after the tinned and soldered specimens had been heated to high enough temperatures to cause the formation of complex copper-tin alloys. Furrowing reduced the strength of soldered joints and impaired markedly the fatigue properties of the copper as measured by the number of bends needed for failure.

Spilt flux may cause pitting of copper, but the pits thus formed occur under deposits of copper salts. A red deposit of cuprous oxide was found under these salt deposits if the copper originally was oxidized.

CONTENTS

	Page
I. Introduction	365
II. Previous work	366
III. Experimental work	367
1. Materials	367
2. Apparatus	368
3. Experimental details	369
(*a*) Tinned copper	369
(*b*) Soldered copper	370
IV. Results	371
1. Tinned copper	371
2. Soldered copper	373
V. Miscellaneous observations and discussion	375
1. Corrosion of copper	375
2. Pitting of tinned copper	376
3. Pitting of soldered copper	377
4. Seam corrosion	377
5. Fluxes	378
VI. Conclusions	378
VII. Acknowledgments	379
VIII. Selected bibliography	379

I. INTRODUCTION

The widespread use of copper for roofing purposes has revealed that improper manipulation of the material can bring about premature failure of the roof. In most instances the cause of failure is obvious, but occasionally it is not so. These occasionally unexplained failures have been the subject of joint investigation by the Copper and Brass Research Association and the Bureau of Standards.

[1] Research associate for Copper and Brass Research Association.

A typical case is illustrated by a sample of sheet copper which had been in service for 16 to 20 years as a valley (fig. 1) in the roof of a residence, and which was sent to the Bureau of Standards for examination. Marked furrowing was observed in the copper along the lower edge of the solder band at those portions not covered by the shingles. No localized corrosion of the copper had occurred along the upper edge, except in the areas where the flow of rain water was greatest. Pits extending through the solder into the copper had formed along the high ridge of the soldered lock seam. Evidence of included flux was obtained upon sectioning the seam. Cavity *D* was found to be filled with liquid, probably flux; likewise, the underside of the seam gave indications that flux had been left in place, although there was no evidence of any deep-seated corrosion having occurred.

Inspection of another old copper roof in the same general geographical region, which is an industrial one and whose atmosphere is corrosive, revealed that the copper on the horizontal, vertical, and sloping parts of a portion of the roof was badly pitted along soldered seams, whereas elsewhere on the same roof there was no evidence of the slightest deterioration of the copper at the seams. The examination of many roofs in a large city where the number of industrial plants is unusually low showed that pitting of the solder is commonplace. The copper exposed at the bottom of such pits was observed to be bright in some cases, and in others covered with patina. In any recess where water could collect along the edge of the soldered seam, or at points where water flowed away from the edge of the soldered seam, the copper was usually leather brown in color, which was different from the predominating color of the sheet. However, furrowing was not found.

When a copper roof is pitted and has an appearance suggestive of wormholes penetrating through it, it seems reasonable to assume that the roof is of tinned copper. The failure of the tinned copper roof on the Library of Congress building in Washington, D. C., has been described by Merica (1).[1] A recent examination made of a specimen of tinned copper of thin gage used for the ornamental work showed as many as 92 pits in an area of a square centimeter after service lasting probably more than a quarter of a century. This is a tremendous increase over that reported before, (1) and is indicative of the influence of bending upon the weathering of tinned copper. Another pitted or "worm-eaten" roof, supposedly of copper, was found to be of tinned copper. The failure of copper roofing by pronounced pitting and furrowing seems quite often to be associated with tin or solder and is the subject of this investigation.

II. PREVIOUS WORK

It appears that no systematic study has been made of furrowing at copper-solder junctions. Merica (1) in his study of the failed tinned copper roofing showed that the tin combined with the copper to form phases known as ϵ' and η (2) which are cathodic to copper, hence, detrimental from the standpoint of corrosion resistance. Dafton and Brady (3) have reported that the corroded areas of tinned copper pipes are cathodic to copper. Lead-tin solder is considered

[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the selected bibliography given at the end of this paper.

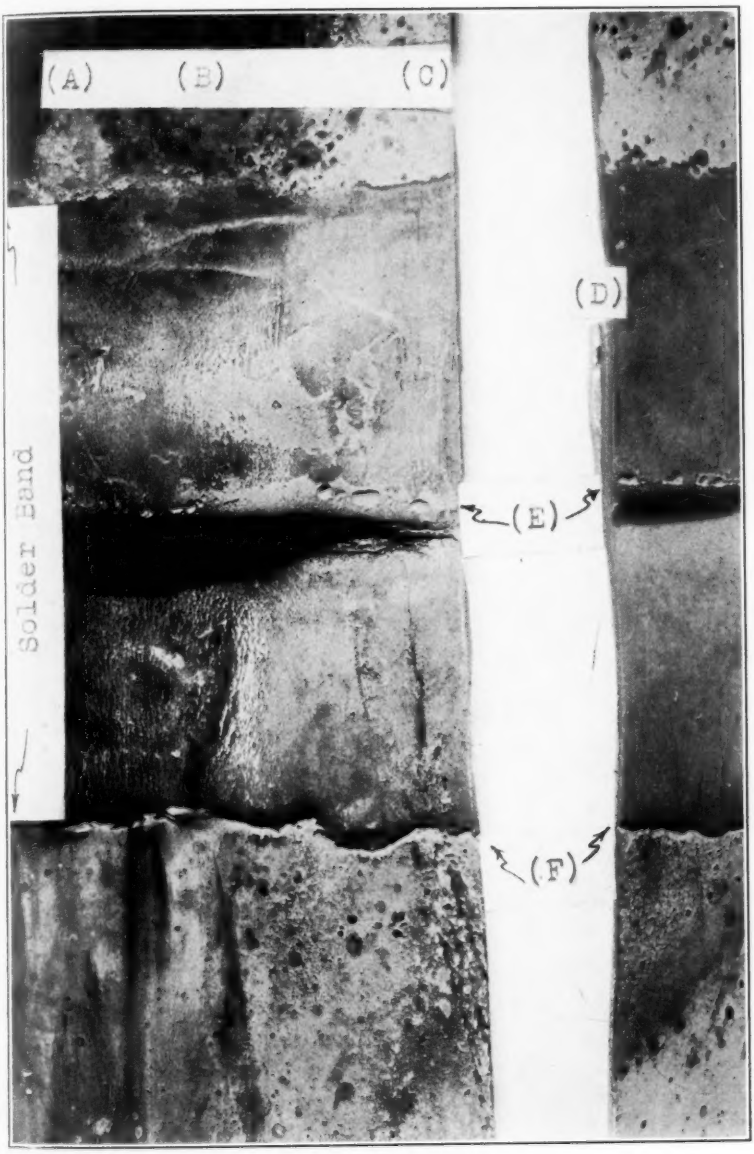


FIGURE 1.—*Seam corrosion on soldered copper valley.* × 2

A, Etched copper where flow of rain water was greatest; *B*, tarnished copper; *C*, patina covered copper where flow of rain water was least; *D*, hole of seam in which flux was trapped; *E*, pits extending through solder at high ridge of seam; *F*, furrow at copper-solder junction.

UNIV. OF MICH.

as being anodic to copper. However, the current (4) set up due to galvanic action has been reported to be small and to decrease with time.

In a study of the metallurgy of soldered copper Crow (5) showed that at temperatures below 300° C. the tin of eutectic solder (63 per cent Sn : 37 per cent Pb) combined with copper to form the ϵ' phase. At temperatures as low as 325° C. the η phase was also formed and appeared as a blue band between the copper and ϵ' layer when examined under a microscope. Weiss (6) obtained the δ bronze phase by holding copper in tin at 550° C. for 24 hours, whereas at 400° C. η was the richest copper phase obtained.

The etching characteristics of the different copper-tin phases have been described by Heycock and Neville (7). Prolonged etching must be carried out to differentiate between them. Crow (5), Merica (1), and also other investigators have reported difficulty in etching.

III. EXPERIMENTAL WORK

1. MATERIALS

Sheet electrolytic copper, 16-ounce gage (nominally 0.0215 inch or 0.055 cm thick) and of roofing temper hardness, was used for the experiments with solder, which was made from equal parts, by weight, of lead and tin. The flux used was made by neutralizing hydrochloric acid (specific gravity 1.18) with zinc, filtering and adding 10 g/l of ammonium chloride. For the work with tinned copper, commercially hand-tinned copper, electrotinned copper, and block tin were used. Table 1 lists the chemical compositions of these materials. The hand-tinned sheets had innumerable fine parallel scratches extending their full length.

TABLE 1.—*Chemical composition of materials*

Mark	Material	Cu	O_2	Fe	Pb	Sn		
						Weight	Average thickness	
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Lbs./100 ft.*[2]	*cm*	*Inch*
1	Electrolytic copper [1]	99.95	0.04					
2	Hand-tinned copper:[3]							
	Copper	99.94						
	Tin coat			(3)	(4)	0.584	0.000392	0.000154
3	Electrotinned copper:[3]							
	Copper	99.956						
	Tin coat			(3)	(4)	.978	.000655	.000258
4	Electrotinned copper:[3]							
	Copper	99.968						
	Tin coat			(3)	(4)	1.772	.00119	.000467
5	Tinned copper:[3]							
	Copper	99.902						
	Tin coat			(3)	(4)	.565	.000378	.000149
6	Solder:[5]							
	Lead				99.99			
	Tin (Straits)[6]	Present.		Present.	Present.			

[1] Manufacturer's analysis.
[2] Analyses by American Brass Co.
[3] Present but in negligible amount.
[4] Not detected.
[5] Solder made from equal parts of lead and tin whose analyses are given.
[6] Spectroscopic analysis.

2. APPARATUS

The accelerated weathering test (8) as used at the Bureau of Standards was utilized in the endeavor to duplicate in the laboratory the weathering of soldered and tinned copper. Figure 2 shows schematically the apparatus which was a modification of that described in the publication just referred to. An industrial atmosphere was simulated by passing a gaseous mixture consisting of 1 per cent SO_2, 5 per cent CO_2, 94 per cent air by volume, into the bottom of

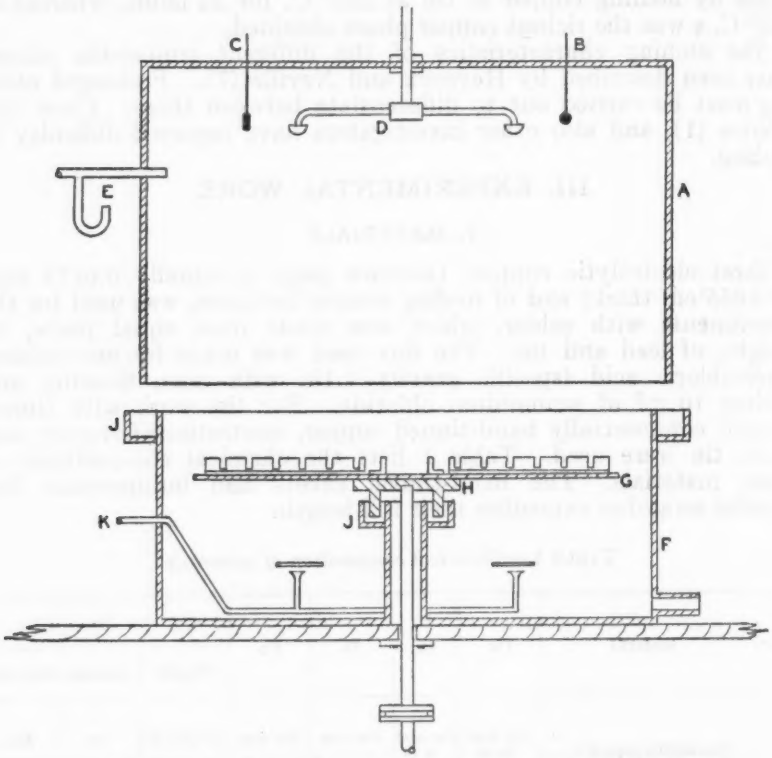


FIGURE 2.—*Apparatus used in accelerated weathering test*

A, upper and movable part of corrosion tank.
B, thermometer
C, thermoregulator.
D, water-sprinkling arrangement.
E, gas outlet.
F, lower part of corrosion tank.
G, specimen rack.
H, rack coupling.
J, water seal.
K, gas inlet.

the corrosion tank, in which there was a layer of 4 inches (10 cm) of water maintained at the specified temperature by electric heaters. The atmosphere was thereby rendered very humid. The specimens were supported on the circular lead-coated aluminum platform, which could be rotated. The shower was used only in the initial tests.

Repeated immersion tests were carried out in equipment already described by Rawdon, Krynitsky, and Finkeldey (9, 10). Beij's (11) solution of 1 *N* sodium chloride and 0.6 *N* sulphurous acid was

employed, evaporation losses being made up by additions of a concentrated sulphurous acid solution containing about 10 g SO_2 in 100 g water. The specimens were supported in glass stirrups and were dipped in the solution for about one-half minute every 15 minutes.

Salt spray tests were carried out. A 20 per cent solution of sodium chloride was atomized in an alberene box by using air at a pressure of 15 lbs./in.^{2} (0.01 kg/mm^2).

Bend tests were made in the machine developed by S. N. Petrenko, of the Bureau of Standards. In this apparatus the specimen was bent, while under tension, around a radius approximately twenty times its thickness, first 90° in one direction and then 90° in the reverse direction. The number of reversals to produce failure was counted.

An Amsler tensile testing machine of 400 pounds (180 kg) capacity was used for determining the tensile properties. Tension specimens with 2-inch (5 cm) gage length were made in accordance with specification E8–27T of the American Society for Testing Materials (1930), with the slight modification that the gradual taper from the ends of the reduced section left in the center a length of one-half inch whose width was 0.500 inch (1.27 cm). This allowed a little leeway in placing the copper-solder junction in the minimum reduced section of the test specimen.

3. EXPERIMENTAL DETAILS

(a) TINNED COPPER

Specimens, 10 cm (3.9 inches) square, of copper, tinned copper, and tinned copper from an old roof were used in the initial test with accelerated weathering. In these and subsequent tests the specimens were polished, washed, dried in alcohol and in ether, and weighed. On some sheets four parallel scratches were made deep enough to expose the copper. After being exposed to the corrosive atmosphere for five hours at 46° to 50° C., the specimens were showered with cold water for one hour. Some specimens were scrubbed with a bristle brush between cycles; others were not. After drying and standing in a desiccator for 18 hours they were weighed before being exposed in the next cycle.

A second series of tests was carried out with soft electrolytic copper, highly polished electrolytic copper, block tin, hand-tinned copper, and electrotinned copper having nominally 1 pound and 2 pounds tin per 100 square feet or 0.00026 inch (0.00066 cm) and 0.00052 inch (0.0013 cm) thick, respectively, on each side. The electrotinned copper specimens were tested in the "as received" condition as well as after heating to 350° C. and to 500° C. The same testing procedure was followed, except that a temperature of 50° C. was maintained, and the specimens were scrubbed between successive cycles. They were weighed at the end of the tenth, twentieth, and thirtieth cycles.

Before testing, all the specimens with the exception of the polished copper ones were rubbed down with No. 000 emery paper. The progress of corrosion was followed by determining the changes in weight and by noting the depth of the pits. Since the same pit

could not be located every time, a number of pits were measured and the maximum depth recorded. The number of pits per unit of area, revealing copper at a magnification of × 6, was counted at each of the four corners of the specimen by means of a template having a square hole 0.5 cm (0.2 inch) on edge.

(b) SOLDERED COPPER

Preliminary work showed that seam corrosion could be duplicated in the same testing apparatus. Copper soldered with half and half solder showed furrowing after accelerated weathering, regardless of whether acid flux or a commercial noncorroding flux was used. Pitting through the solder occurred wherever the solder was thin.

Strips of electrolytic copper, 8 by 20 cm (3 by 8 inches), were dipped in flux and then in molten solder which was kept at 270° C. in a nichrome-wire wound carbon block trough 15 cm (6 inches) deep. The drop in temperature during the 1-minute soldering period did not exceed 5°. Some specimens of plain and soldered copper were annealed at 500° C. under charcoal for three hours and then air cooled.

After being rubbed down with No. 0 emery paper, washed, dried, and weighed, sets of specimens were acceleratedly weathered for 200 hours at 40° C., 200 hours at 50° C., and 90 hours at 60° C. They were removed from the corrosion tank twice a day, at the end of runs whose duration was alternately 6½ and 16½ hours, sprayed with hot water for five minutes, allowed to dry, and then replaced. This procedure did not as seriously alter the testing conditions within the tank as above described (p. 369) and allowed corrosion to be continued throughout the entire day (24 hours). At the end of every 100 hours the specimens were scrubbed with a bristle brush and water and reweighed. After being weighed at the end of 200 hours' exposure they were reweighed after being given five half-minute dips in 15 per cent (by weight) sulphuric acid, which removed all products of corrosion without appreciably attacking the uncorroded portions.

Strips for tensile and bend tests were cut from these acceleratedly weathered specimens. Determinations were made of the ultimate tensile strength, per cent elongation in 2 inches (5 cm) of which 1 inch (2.5 cm) was soldered copper, and the number of reversals to produce failure when under tensions of 4,000 and 1,000 pounds per square inch (2.8 and 0.70 kg/mm^2).

The specimens for metallographic examination were first copper-plated and then mounted for polishing in one of the following: Wood's metal, Canadian balsam, tin, and half-and-half solder. Oblique surface sections were obtained by slightly bending the specimen before mounting and polishing on the convex side (1). An etching reagent of ammonium hydroxide and hydrogen peroxide was used for revealing the structure of the copper, and an acid ferric chloride solution, as well as nitric acid with chromium oxide additions, for revealing the structure of the coating. The galvanic action between the copper and the coating interfered with uniform etching. Polishing was difficult on account of the gouging out of the soft coating.

IV. RESULTS

1. TINNED COPPER

The appearance of the specimens of hand-tinned copper after accelerated weathering was somewhat comparable with that after outdoor weathering, the surface being dulled and discolored, often with a greenish tinge. The discolored areas were plainly etched and pitted. The greatest corrosive attack occurred along the multitude of fine scratches. No marked peculiarity was noticed on the deep scratches which revealed copper. The specimens with the thinnest tin coat suffered the most corrosion, as judged both by appearances and losses in weight. The specimens of the old tinned copper roofing, which were included in the test, showed very high corrosion rates. Table 2 lists the results of this initial test. The losses in weight are given in g/dm²/cycle for the first, fifth, and tenth cycles, as well as the average for the 10 cycles. The time required till the first appearance of copper through the coating in areas away from the edge of the specimen was taken as the time of failure.

TABLE 2.—*Initial accelerated weathering test of tinned sheet copper*

AS RECEIVED

Scrubbed after each cycle

Specimen	Corrosion rate—g/dm²/cycle				Time to fail (cycle number)
	First cycle	Fifth cycle	Tenth cycle	Average of 10 cycles	
5-1	0.0001	0.0050	0.0020	0.0020	Fifth.
5-2	.0002	.0038	.0021	.0020	Fourth.
5-3	.0000	.0019	.0018	.0016	Fifth.
Not scrubbed after each cycle					
5-7				0.0006	No failure.
5-8				.0008	Do.
SCRATCHED SPECIMENS					
Scrubbed after each cycle					
5-4	0.0002	0.0011	0.0020	0.0013	No failure.
5-5	.0001	.0047	.0026	.0020	Fifth.
5-6	.0003	.0090	.0045	.0048	Fourth.
Not scrubbed after each cycle					
5-9				0.0002	No failure.
5-10				.0003	Do.
Tinned copper from old roof					
L-1				0.0039	
L-2				.0062	

It was difficult to obtain duplicate corroding conditions within the tank from one run to the next. This can be attributed in part to the use of the cold-water shower, which immediately removed all traces of sulphur dioxide gas from the atmosphere. It was known that considerable time was required before the composition of the gas mixture within the tank became uniform.

Table 3 lists the results obtained from the second accelerated weathering test. The adherent films which formed on the copper were slightly soluble in water but were removable only by pickling. The presence of copper ions and sulphate ions was detected in the wash water used in scrubbing the specimens. Under the microscope, green specks were discernible on the surface of the scrubbed copper, but the general appearance was dark brown or black. Green patina formed in time, especially on the specimens not scrubbed between cycles.

TABLE 3.—*Second accelerated weathering test of plain and tinned sheet copper*

Material		Coating			Cycle period	Corrosion rate			Pitting		Time of failure (cycle number)
Mark	Treatment	Weight	Thickness			Maximum	Minimum	Average	No./cm²	Maximum depth	
			Maximum	Minimum							
		lbs./100 ft.²	*cm*	*cm*		*g/dm²/10 cycles*	*g/dm²/10 cycles*	*g/dm²/10 cycles*		*cm*	
Copper.	Soft electrolytic	None			1–10	0.19	0.16	0.177			
					11–20	.14	.09	.117			
					21–30	.082	.066	.074			
	Polished	None			1–10	.20	.17	.186			
					11–20	.11	.10	.102			
					21–30	.076	.042	.062			
2	Hand tinned	0.584	0.001	0.0002	1–10	.105	.048	.073		0.0013	1-2
					11–20	.073	.040	.052		.0053	
					21–30	.059	.039	.051	10	.0079	
3	Electrotinned	.978	.0014	.0004	1–10	.011	.0065	.0085			6
					11–20	.012	.010	.012		.0051	
					21–30	.023	.013	.017	4	.0081	
4	Electrotinned	1.772	.010	.0017	1–10	.0101	.0071	.0089			10
					11–20	.0096	.0066	.0079			
					21–30	.013	.011	.012	1	.0038	
4-3	Electrotinned and heated to 350° C.				1–10	.060	.049	.055		.0046	1
					11–20	.038	.026	.030		.0071	
					21–30	.032	.026	.029	10	.0102	
4-5	Electrotinned and heated to 500° C.				1–10	.108	.082	.095		.0043	1
					11–20	.103	.048	.071		.010	
					21–30	.115	.077	.096	22	.010	
Tin.	Sheet	None			1–10	.0064	.0012	.031			
					11–20	.0039	.0021	.027			
					21–30	.0044	.0037	.040			

Visual observation showed that thin oxide films on copper, such as are formed when the copper is heated at 100° C., tended to retard corrosion during the initial periods of weathering. However, thicker films did not show this tendency, probably on account of their cracking. In Table 5 it is shown that the oxide films of negligible weight produced at 130°, 170°, and 500° C. were accompanied by greater corrosion losses. The set of specimens which was weathered at 60° C. was oxidized for a longer period of time than that weathered at 50° C. and, therefore, having a thicker oxide film, suffered greater corrosion.

The surface of the hand-tinned copper was dulled and discolored. all had long, parallel, brown or yellow streaks speckled with black;

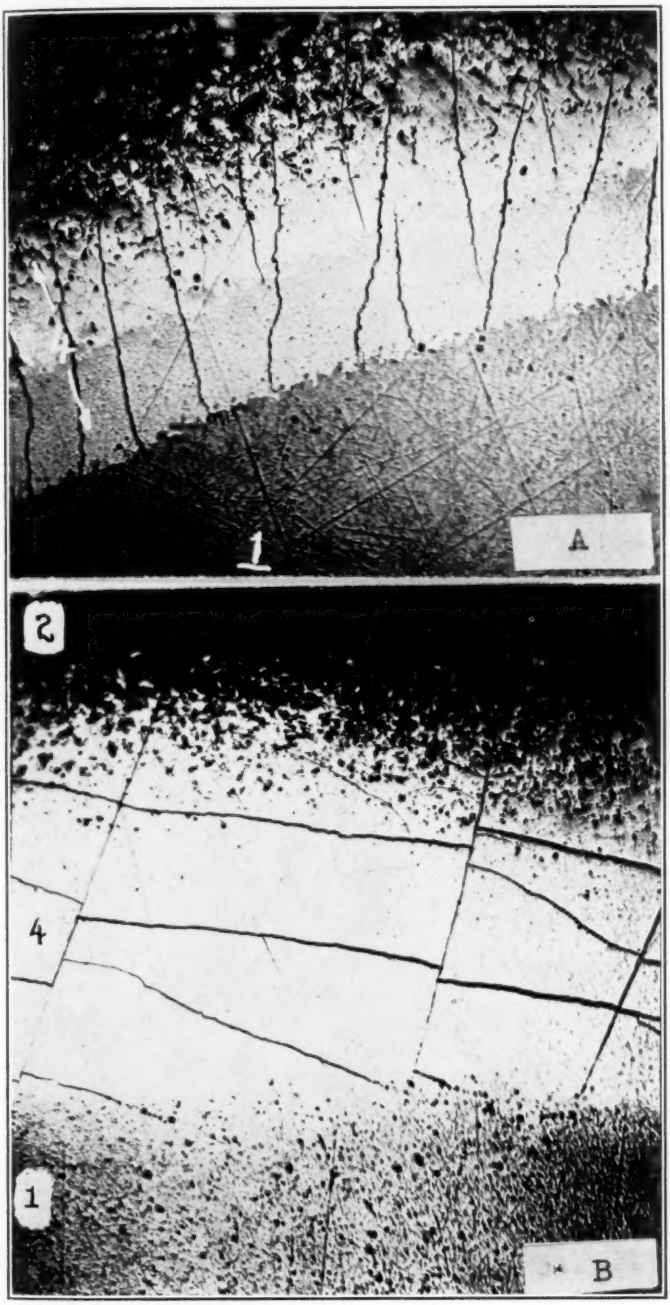


FIGURE 3.—*Oblique sections of heat treated electrotinned sheet copper showing cracks in coating.* × *100*

A, Heated to 350° C.; *B*, heated to 500° C. *1*, Sheet copper base; *2*, unchanged tin; *4*, copper-tin alloys. Both unetched.

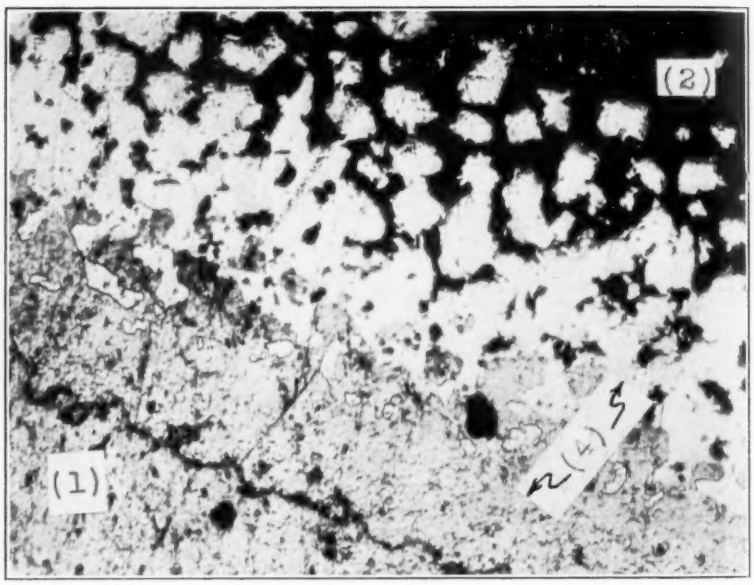


FIGURE 4.—*Oblique section of electrotinned sheet copper heated to 350° C. for three hours.* × *500*

Etchant: Nitric acid. *1*, Sheet copper base; *2*, unchanged tin; *4*, copper-tin alloys.

Accidental scratches were badly discolored. Electrotinned copper was stained considerably but was not streaked like the hand-tinned copper. It resembled the sheets of block tin. Considerable edge corrosion occurred, the tin being removed. The failure of the coating was greatly facilitated by the heating of electrotinned copper to a temperature above the melting point of the tin, the appearance of the pitted areas being similar to that of the old out-doors-weathered tinned copper. The specimens of block tin were tarnished and speckled with dark and light brown spots. The indications were that its corrosion rate tended to increase with time.

The microstructure of the coatings on heat-treated electrotinned copper was rather complex. Electrotinned copper had but one phase present in the coating—the tin. Upon heating to 350° and 500° C., the copper and tin alloyed, copper dissolving quite rapidly in the tin. The alloy layers were brittle and slight bending caused them to crack, as shown in Figure 3. Many of these cracks extended through the alloy layer only. During polishing a slight relief effect was sometimes obtained, as shown in Figure 3(*a*), thus revealing the complex nature of the coating.

At least two phases were distinguishable in the alloy layer formed at 350° C. In Figure 4, next to the copper is a dove gray layer, and next to it is a brilliantly white layer. Patches of unchanged tin etched dark. Particularly good contrast was obtained in this figure by leaving the specimen over night in the laboratory atmosphere.

By heating to 500° C. another phase was formed which tarnished brownish on etching. This phase and the dove gray and brilliant white phases noted above are to be seen in Figure 5. In one place only, not shown, was the needlelike structure with a brilliant white fringe found to have a definitely blue color, characteristic of the η phase. It is assumed that the brownish phase is δ, the brilliant white ϵ' and the dove gray η.

The salt spray test appears to be a very slow method for producing failure of tin coating on copper. After 1,000 hours' exposure, only a slight difference between handtinned and electrotinned specimens was noticeable, the former showing spots of bare copper and the latter not. The time of the first appearance of these bare spots could not be determined.

2. SOLDERED COPPER

In Tables 4 and 5 and in Figure 6 are given the results of accelerated weathering of soldered copper. At the end of the first 100-hour period many of the specimens were found, after scrubbing, drying, and weighing, to have increased in weight, and after 200 hours very slight losses were noticeable. However, after removing the corrosion film by pickling considerable loss in weight was observed. The reported corrosion rates for soldered copper were calculated on the assumption that all the loss was from the bare copper portion whose area was very nearly 50 per cent of the total area exposed. These figures indicate that the corrosion rate of soldered copper increased with increase in annealing temperature to which the solder was subjected.

TABLE 4.—*Tensile properties of plain and soldered sheet copper before and after accelerated weathering*

Material		Before weathering		After weathering					
				200 hours at 40° C.		200 hours at 50° C.		90 hours at 60° C.	
Mark	Treatment	Tensile strength	Elongation	Tensile strength	Elongation	Tensile strength	Elongation	Tensile strength	Elongation
		Lbs./in.²	*Per cent*	*Lbs./in.²*	*Per cent*	*Lbs./in.²*	*Per cent*	*Lbs./in.²*	*Per cent*
1 Cu	Roofing temper	32,900	41	31,700	36	32,200	39	33,200	39
1 Cu	Annealed at 500° C	32,000	40	32,400	43	31,500	35	32,300	39
1 Cu	Soldered	32,800	37	32,700	38	32,700	36	32,800	36
1 Cu	Soldered and annealed at 500° C	32,300	33	32,300	29	31,000	23	31,600	24

NOTE.—All figures are average of three determinations.

TABLE 5.—*Weight losses of plain and soldered sheet copper when subjected to accelerated weathering*

Material		Weight loss (g/dm² of copper)								
		200 hours at 40° C.			200 hours at 50° C.			90 hours at 60° C.		
Mark	Treatment	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
1 Cu	Roofing temper	0.36	0.27	0.30	0.574	0.465	0.53	0.55	0.52	0.54
1 Cu	Annealed at 500° C	.35	.30	.33	.807	.624	.72	.57	.54	.56
1 Cu	Soldered	(.43)	(.21)	(.31)	(.567)	(.548)	(.56)	(.60)	(.57)	(.59)
1 Cu	Soldered and annealed at 500° C	(.37)	(.33)	(.36)	(.925)	(.912)	(.92)	(.77)	(.77)	(.77)
1 Cu	Surface oxidized at—									
	130° C						.51	.70	.64	.67
	170° C						.58	.64	.64	.64
	500° C				.997	.778	.89			

NOTE.—Figures in parentheses were calculated on the assumption that all weight lost was from the bare copper portion whose area was measured and which was very nearly 50 per cent of total area exposed.

The physical appearance of the specimens after corrosion is shown in Figures 7 to 10. Figure 9 is a magnified view of the furrowing which is especially in evidence in the A specimen; the B specimen shows, on the other hand, very slight attack.

After weathering, three phases were distinguished on these soldered and annealed specimens. Figure 10 shows the appearance of these phases and illustrates the association of pits with them. Areas C and B are evidently the δ and η phases and A the unchanged solder.

The characteristic microstructures of the soldered specimens are shown in Figures 11 to 13. Figure 12 shows the cracks in the very thick coating of copper-tin alloys on soldered and annealed copper. The black line between the copper and the alloys resulted from the deep etching of the copper, which is anodic to the coating in ammonium hydroxide.

The repeated immersion tests did not exactly duplicate the furrowing of copper at copper-solder junctions. After 200 hours a plain copper specimen was coated with a uniform green film except at points of contact with the glass stirrups and at the bottom, which had a knife-blade edge. The solder of soldered-copper specimens was

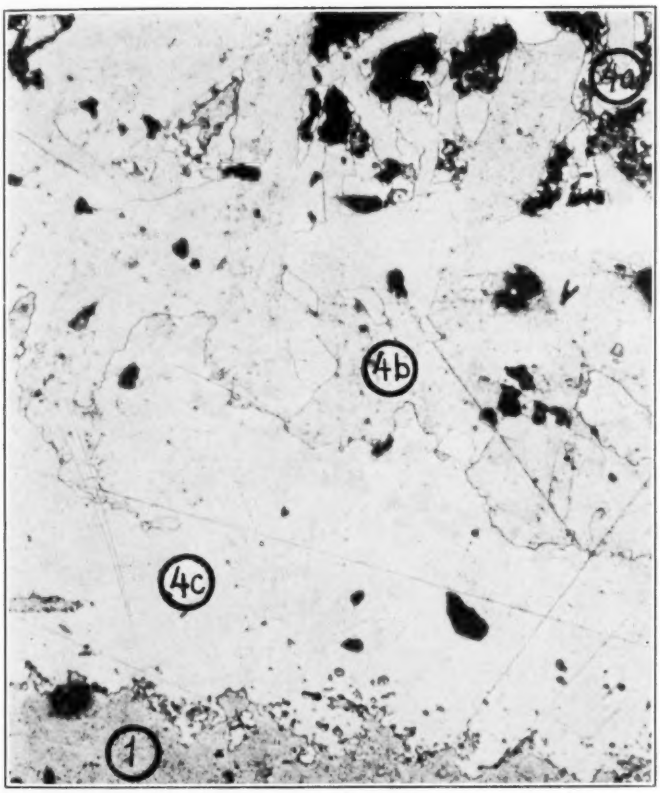


FIGURE 5.—*Oblique section of electrotinned sheet copper heated to 500° C. for 3 hours.* × *200*

Etchant: Concentrated nitric acid. *1*, Sheet copper base; *4a*, brilliant white ϵ' phase; *4b*, bluish η phase; *4c*, brownish δ phase.

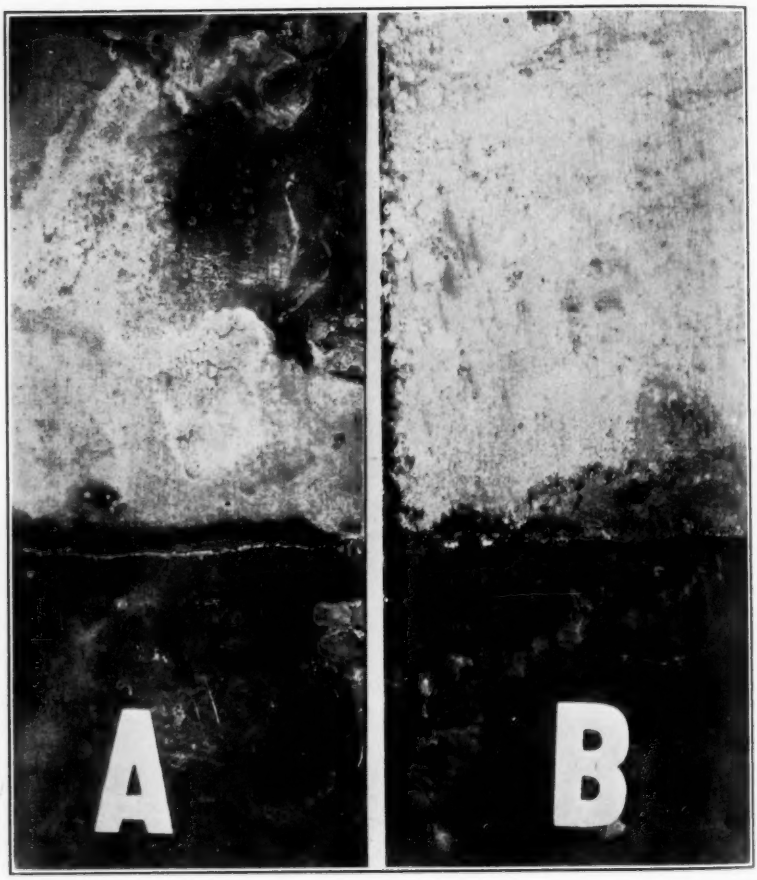


FIGURE 7.—*Seam corrosion after 100 hours accelerated weathering at 50° C.* × *0.7*

The surface has been scrubbed with bristle brush and water. *A*, Soldered at 270° C. and heated to 500° C.; *B*, soldered at 270° C. Lower half is copper, upper half is solder covered

badly corroded and did not appear to have accelerated the corrosion of the copper. However, copper soldered at 270° C. and annealed at 500° C. was badly attacked. There was no marked evidence of furrowing at the copper-solder junction as is obtained in accelerated weathering, but the copper was uniformly dissolved away. This left a pronounced shoulder at the junction. The soldered-covered portion was badly pitted and perforated. The pits had white walls and were always to be found in light-blue areas. Most of the solder had been dissolved away.

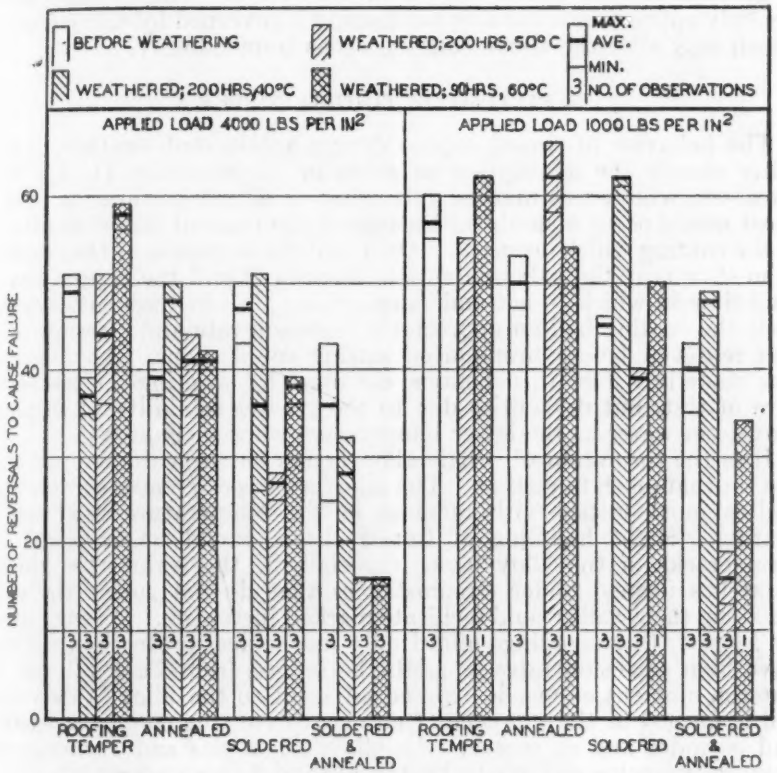


FIGURE 6.—*Results of bend tests of plain and soldered sheet copper*

V. MISCELLANEOUS OBSERVATIONS AND DISCUSSION

1. CORROSION OF COPPER

English investigators (12) of the atmospheric corrosion of copper have shown that copper sulphate is a common corrosion product found on copper roofs. The finding in these laboratory tests, reported herein, of water-soluble corrosion products with traces of the sulphate ion is consistent with Vernon's observations.

Intercomparisons of the corrosion rates of copper given in Tables 3 and 5 show that after 30 cycles or 150 hours of exposure to the gas mixture, copper lost a total of 0.368 g/dm², equivalent to a loss of 0.47 g/dm² in 190 hours. This is comparable with 0.53 g/dm² for

copper of similar temper when continuously exposed to the corroding gas at 50° for 200 nominal hours, of which actually 10 hours were used for washing and drying outside of the tank. Average penetration figures equivalent to these corrosion rates are 0.00053 cm and 0.00060 cm, respectively. If 0.0001 inch (0.00025 cm) per year be taken as an average outdoor corrosion rate of copper (13, 14, 15, 16) then 200 hours continuous accelerated weathering approximates two years natural weathering. This agrees qualitatively at least with the fact that the depth of furrowing after accelerated weathering is not so great as outdoor weathering for 16 to 20 years. These comparisons are only approximate because weathering is governed by many factors which may alter the above considerations tremendously.

2. PITTING OF TINNED COPPER

The behavior of tinned copper during accelerated weathering fits fairly closely the description as given in the literature (1, 17, 18). However, whether as marked furrowing or actual perforation of the sheet would occur is doubtful because of the marked chemical attack of the coating which occurred. On a roof the corrosion of the coating is so slow that the galvanic action between it and the copper has a long time in which to act and cause pitting, but in these accelerated tests the coating had an appreciable corrosion rate and consequently was removed before pronounced pitting could occur. An attempt was made to reduce this chemical corrosion by lowering the temperature of test, but difficulties due to the greater solubility of sulphur dioxide in water at the lower temperature were encountered.

It is the formation of brittle alloy layers between the copper and the tin that leads to pitting. The alloy layer is of greater complexity and is more brittle with increase in the temperature used while coating. Slight handling of tinned sheets would be sufficient to form cracks in the alloy layer, especially if the layer were thick. Scratches formed under circumstances that do not smear the soft tin along their walls would facilitate marked furrowing. As suggested by Merica, these coatings afford only mechanical protection. They have high corrosion rates as might be judged from Tables 2 and 5, but the moment copper is exposed adjacent to the alloy, a galvanic cell is formed in the presence of an electrolyte; the copper is anodic and corrodes and so protects the alloy. The pits and furrows can grow in diameter and width by the coating being undercut, leaving the brittle alloy unprotected and thus subject to further corrosion.

The incompleted preliminary studies of the polarity of these alloys with respect to copper showed that in agitated solutions the copper was anodic to the different phases present in the tin coat and exposed by corrosion. This is in accordance with the observations of Merica, especially in sulphate solutions. Examination of the roof of the Library of Congress revealed that the furrows and pits were much larger on the dome roofing than on small pieces of tinned copper that had fallen from ornaments and lain for an indefinite period on flat portions of the roof. It should be expected that the difference in velocity between rain water flowing down over the dome and that flowing over the loose pieces lying on the flat roof would be considerable. Comparison with the tinned copper of flat decks on the roof was not possible because the roof had been painted. In Figure 1

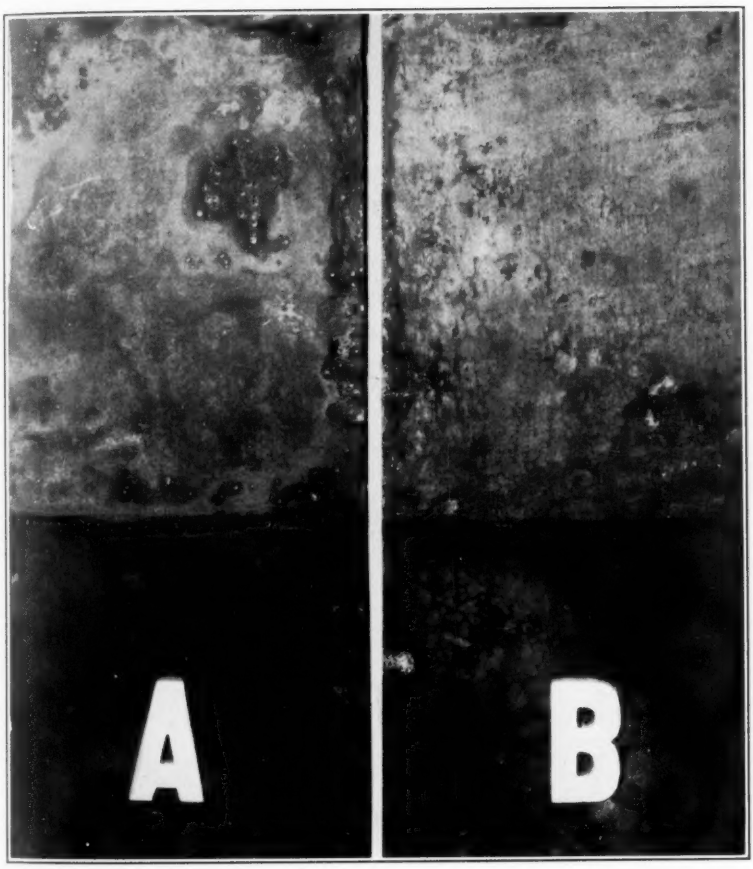


FIGURE 8.—*Same as Figure 7, but after 200 hours accelerated weathering at 50° C.* × *0.7*

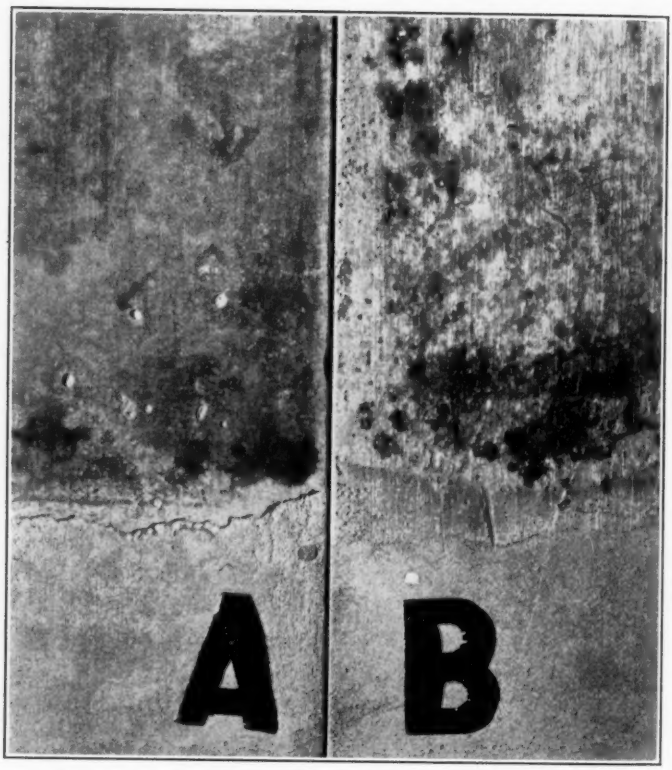


FIGURE 9.—*Same as Figure 8, but after pickling.* × 3.7

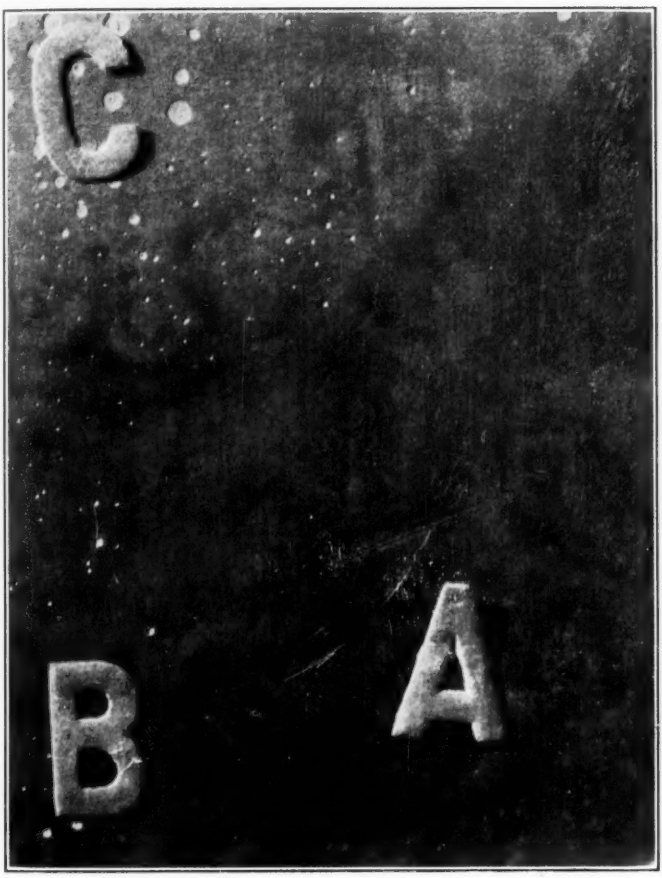


FIGURE 10.—*Phases on acceleratedly weathered soldered copper*

A, Dull gray with no pits; *B*, blue gray with a few pits; *C*, white gray with many pits.

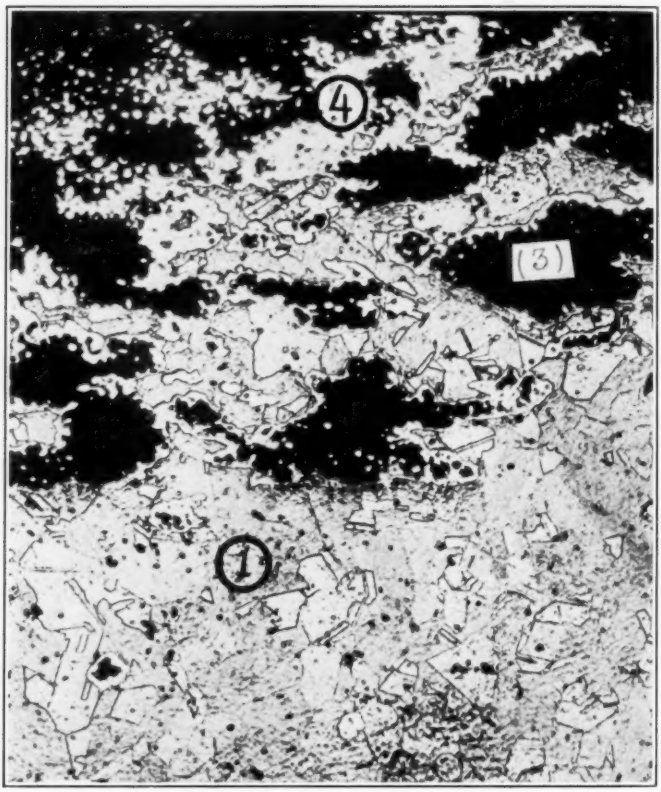


FIGURE 11.—*Oblique section of sheet copper soldered at 270° C.* $\times$ *500*

Etchant: $NH_4OH+H_2O_2$. *1*, Sheet copper base; *3*, unchanged solder; *4*, ϵ' phase.

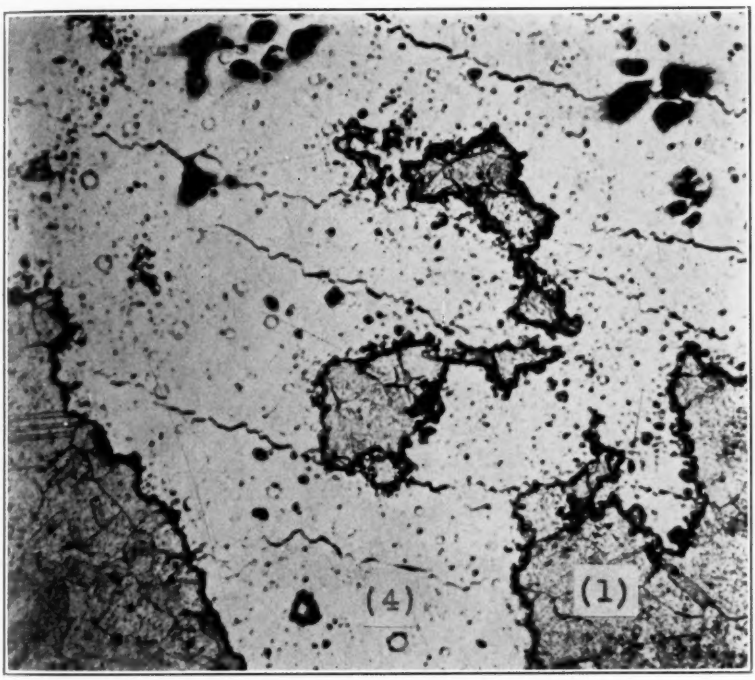


FIGURE 12.—*Oblique section of sheet copper soldered at 270° C. and heated to 500° C. for 3 hours.* × *500*

Etchant: $NH_4OH+H_2O_2$. *1*, Sheet copper base; *4*, copper-tin alloys.

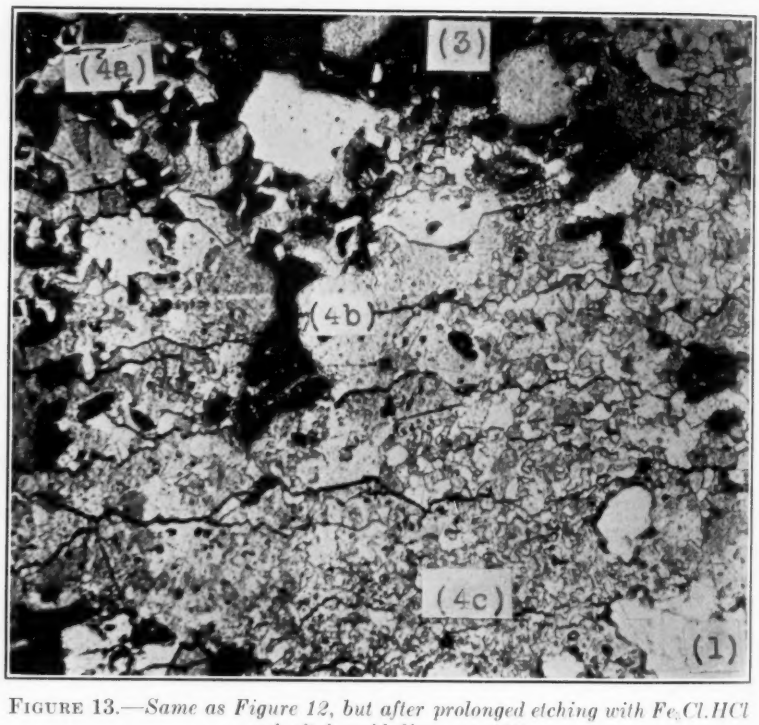


FIGURE 13.—*Same as Figure 12, but after prolonged etching with $Fe_2Cl.HCl$ and nitric acid dip.* × *200*

1, Sheet copper base; *3*, unchanged solder; *4a*, bright areas of ϵ' phase; *4b*, η phase; *4c*, δ phase.

there is noticeable the etching of copper adjacent to solder in areas where the flow of rain water was considerable.

3. PITTING OF SOLDERED COPPER

Pitting of soldered copper is another example of the pitting of copper which has been coated with a metallic alloy containing tin. The usual place to find such pits is the uppermost ridge of the seam—the place that would be the first to be touched by the soldering iron, that receives the wear and tear, and that would be expected to have the thinnest coating of solder. The specimens of hand-tinned copper which were judged to have the thinnest coating also suffered the most corrosion. Pits formed during the soldering process are akin to blowholes. They are those pits which have patina-covered copper on the bottom.

Nightingale (19) and Beij (20) and others have shown that the strongest soldered joint has but little solder between the copper members and that piling up heavy wide bands of solder on flat lock seams to increase their strength is not worth while. However, from the point of view of corrosion resistance, a moderate amount of solder which completely covers the copper-tin alloys is beneficial in preventing the pitting of copper. It does not seem possible to prevent seam corrosion by such a procedure.

4. SEAM CORROSION

The influence of the temperature of soldering on seam corrosion which is another example of detrimental galvanic corrosion of copper by copper-tin alloys is shown by the change in the physical properties upon weathering, especially of the soldered and annealed specimens weathered for 200 hours at 50° C. The tensile strength of one individual specimen was lowered as much as 3,000 lbs./in.^{2} due to accelerated weathering. The greatest change was in the number of bends needed to produce failure.

The bend test is essentially a severe fatigue test, though the results obtained from such tests are empirical in nature and difficult to apply to everyday service. When copper is used for roofing purposes it may be subjected to repeated bending through small angles, especially if it is so anchored that the ends of a long stretch can not slide, and expansion and contraction results in buckling and stressing. At points where the copper is stiffened, as by the use of solder, the bending will tend to occur at the copper-solder junction. The results given in Figure 6 show that weathering has a pronounced effect on the fatigue properties of such a joint, as measured in terms of the number of bends to produce failure, and that the weathering effect is greater the higher the temperature to which the solder is subjected. Experienced sheet-metal workers are confident that their joints will not pit and furrow. Such men advocate the use of soldering irons at low temperatures. It is a pity that the poor workmanship of novices is not revealed before a whole decade passes. It is probably their work that accounts for seam corrosion occurring on a small portion of some roofs, the soldering on the other portions being done by experienced men and showing no signs of corrosion at the end of a decade. The use of eutectic solder which would permit soldering at lower temperatures might be beneficial.

5. FLUXES

The matter of fluxes is still a problem. Though flux is not responsible for the seam corrosion nor for the pitting of copper covered with tin-bearing metals, carelessness in handling the flux can cause damage. Drops of any solution, such as sodium chloride or "killed" acid flux, which can form insoluble copper salts, will cause pitting of the copper if allowed to remain on it (21). For instance, drops of sodium-chloride solutions whose concentration is $N/100$ or stronger, formed in their center a deposit of insoluble basic copper chloride when allowed to stand on copper under conditions which prevented evaporation. The maximum depth of pitting measured in tests extending over five weeks was found to have been reached in the third to fourth week and was of the order of 0.004 inch (0.01 cm). Some scratches which passed through this copper-chloride deposit were enlarged, usually by a continuous series of pits along them. Heating copper to 100° C. for an hour, causing the formation of oxide film, resulted in wider and deeper pits being formed under drops of salt solution. A porous red deposit, believed to be cuprous oxide, was found underneath the green deposit in the pitted areas.

When solutions of zinc chloride, which are representative of flux, were used instead of sodium chloride solutions, the same phenomenon occurred, only the copper was pitted to a greater degree. A concentrated solution of zinc chloride was more destructive than a dilute one. Laboratory experiments showed that improperly killed flux was more destructive to copper than zinc chloride solutions.

These deposits under which pitting occurred were not removable by a strong stream of water. It is therefore unwise to be careless when using killed acid flux and depend upon rain to wash any spilt or excess flux from the roof. This is especially so during summer months when much repair work is done on roofs, because of the possibility of extended periods of drought, during which the pitting may get started and the adherent films will not be washed away.

VI. CONCLUSIONS

Accelerated weathering tests with a humid-gas mixture of 1 per cent SO_2, 5 per cent CO_2, 94 per cent air at temperatures above 50° C., were made, in which were duplicated the pitting of tinned copper and the furrowing of copper at a copper-solder junction such as occasionally occurs in copper-roofing material during service. The phenomenon is associated with the formation of copper-tin alloys at the junction of the copper with the tin or solder. These alloy layers are brittle, and cracks are easily formed; the exposed copper forms the anode of a galvanic cell with the alloy in the presence of suitable solutions and is corroded. The higher the temperature used for tinning or soldering the greater is the tendency for pits and furrows to form by subsequent corrosion. The prevention of the formation of such alloys removes the tendency of the soldered copper to pit and to furrow.

The effect of seam corrosion is to reduce the strength of soldered joints and to impair markedly the fatigue properties of the copper as measured in terms of the number of bends required to produce failure.

Spilt flux, if left in place, causes pitting of copper. This pitting occurs under very adherent deposits of copper salts which are not

removable by water. The presence of thin oxide films on copper brings about deeper pitting. In such cases, when sodium-chloride solutions are used, porous cuprous-oxide deposits are found under the layer of copper salts which causes the pitting.

VII. ACKNOWLEDGMENTS

This work could not have been carried out without the full cooperation of all members of the metallurgical division of the Bureau of Standards, especially of E. C. Groesbeck. H. H. Walkup built the new accelerated weathering apparatus and calibrated the flow meters. Thanks are due the Copper and Brass Research Association and its member companies for their material assistance and interest in the work.

VIII. SELECTED BIBLIOGRAPHY

1. P. D. Merica, Structure of the Coating on Tinned Sheet Copper in Relation to a Specific Cause of Corrosion, B. S. Tech. Paper No. 90, 1917.
2. Tin-Copper Equilibrium Diagram, National Metals Handbook, Am. Soc. Steel Treating, p. 771, 1930; Metal Progress, vol. 18, No. 3, p. 114, September, 1930.
3. A. C. Dafton and F. L. Brady, Corrosion of Copper Pipes, Nature, vol. 20, p. 367, 1927.
4. U. R. Evans, Corrosion of Metals at Joints and Crevices, J. Roy. Soc. Arts, vol. 75, p 544, 1927.
5. T. B. Crow, Some Properties of Soft Soldered Joints, J. Soc. Chem. Ind., vol. 43, p. 65T, 1924. Some Experiments on the Soft Soldering of Copper, J. Inst. Met., vol. 35, No. 1, p. 55, 1926.
6. J. Weiss, Introduction to the Study of Metallic Cementation, Revue de Metallurgie, vol. 21, p. 18, 1924.
7. C. T. Heycock and F. H. Neville, The Constitution of the Copper-Tin Series of Alloys, Phil. Trans. Roy. Soc. Series A, vol. 22, p. 1, 1904.
8. E. C. Groesbeck and W. A. Tucker, Accelerated Laboratory Corrosion Test Methods for Zinc Coated Steel, B. S. Jour. Research, vol. 1, p. 255, 1928.
9. H. S. Rawdon, A. I. Krynitsky, and W. H. Finkeldey, Types of Apparatus Used in Testing the Corrodibility of Metals, Proc. A. S. T. M., vol. 24, p. 717, 1924.
10. H. S. Rawdon, Corrosion Embrittlement of Duralumin, II. Accelerated Corrosion Tests and the Behavior of High Strength Aluminum Alloys of Different Compositions. Tech. Note No. 283, N. A. C. A., April, 1928.
11. K. H. Beij, Corrosion of Open-Valley Flashings, B. S. Jour. Research, vol. 3, p. 937, 1929.
12. W. H. J. Vernon, A Laboratory Study of the Atmospheric Corrosion of Copper, Trans. Faraday Soc., vol. 27, p. 255, 1931. Open Air Corrosion of Copper, J. Inst. Met., vol. 42, p. 181, 1929; vol. 44, p. 389, 1930.
13. W. H. J. Vernon, Atmospheric Corrosion of Metals, Trans. Faraday Soc., vol. 19, p. 839, 1924.
14. J. C. Hudson, Atmospheric Corrosion of Metals, Trans. Faraday Soc., vol. 25, p. 177, 1929.
15. J. C. Hudson, Effects of Two Years' Atmospheric Exposure in the Breaking Load of Hard Drawn Nonferrous Wires, J. Inst. Metals, vol. 44, p. 409, 1930.
16. J. N. Friend, Relative Corrodibilities of Ferrous Alloys and Nonferrous Metals and Alloys, J. Inst. Met., vol. 42, p. 149, 1929.
17. T. Appleton, Tin and Copper Roofing, J. Soc. of Constructors of Federal Bldgs., vol. 4, p. 183, 1913.
18. E. G. Schweig, Roofing Comment, J. Soc. of Constructors of Federal Bldgs., vol. 4, p. 402, 1913.
19. S. J. Nightingale, The Joining of Metals, Brit. Non-Fer. Metals Res. Assoc., Res. Rep. No. C234/214, December, 1929.
20. K. H. Beij, Seams for Copper Roofing, B. S. Jour. Research, vol. 5, p. 585, 1930.
21. U. R. Evans, The Corrosion of Metals, Ed. Arnold & Co., 1924.

WASHINGTON, December 30, 1931.

THE CHROMIUM OXIDE AND THE VANADIUM OXIDE BAND SPECTRA

By W. F. C. Ferguson [1]

ABSTRACT

With the aid of much more extended measurements on the band heads due to chromium oxide (CrO) and to vanadium oxide (VO) more complete and precise vibrational analyses were made of these spectra. The new equations, representing band heads are found to be:

CrO: $\nu = 16{,}594.6 + 746.9\ (v' + \tfrac{1}{2}) - 7.9\ (v' + \tfrac{1}{2})^2 - 897.5\ (v'' + \tfrac{1}{2}) + 6.55\ (v'' + \tfrac{1}{2})^2$;

VO: $\nu = 17{,}498.8 + 864.9\ (v' + \tfrac{1}{2}) - 5.70\ (v' + \tfrac{1}{2})^2 - 1{,}012.3\ (v'' + \tfrac{1}{2}) + 5.27\ (v'' + \tfrac{1}{2})^2$.

Additional unassigned bands of VO are listed.

CONTENTS

	Page
I. Chromium oxide	381
II. Vanadium oxide	382

I. CHROMIUM OXIDE

The band spectrum of chromium oxide, CrO, is emitted by an arc containing chromium, in air. Measurements of several band heads have been made by Eder and Valenta,[2] and others,[3] and more recently by Kiess and Meggers.[4] A vibrational analysis of part of the older data was made by Mecke.[5] In view of the meager data used in that analysis it seemed well to extend the observations of the band heads as far as possible and make a more precise determination of the vibrational constants of the molecule.

The spectrum was obtained by introducing pure chromium metal into a carbon arc. Photographs were taken with low dispersion (about 60 A per mm at 6,600 A) on a Hilger E2 spectrograph using one glass 60° prism. Wratten and Wainwright panchromatic plates and especially dyed Eastman 33 plates were used for the visible and infra-red regions of the spectrum, to 9,000 A.

All the band heads that could be measured with certainty were found to belong to the system originally identified by Mecke,[6] all bands shaded toward longer wave lengths. The intensity distribution among the bands follows a typical Condon[7] parabola. The

[1] Assistant professor of physics, New York University. This work was done as guest at the Bureau of Standards.
[2] Eder and Valenta, Atlas Typischer Spektren, Wien, 1911.
[3] Kayser, u. Konen, Handb. d. Spect., vol. 7, p. 306, 1924; for VO: H. Kayser, Handb., vol. 6, p. 786, 1912.
[4] Kiess and Meggers, B. S. Scic. Paper No. 372, 1920.
[5] Mecke, Phys. Zeit., vol. 28, p. 514, 1927.
[6] Mecke, Phys. Zeit., vol. 28, p. 514, 1927.
[7] Condon, Phys. Rev., vol. 28, p. 1182, 1926.

revised equation which represents the positions of all band heads within observational errors is

$$\nu = 16{,}594.6 + 746.9\ (v' + \tfrac{1}{2}) - 7.9\ (v' + \tfrac{1}{2})^2 - 897.5\ (v'' + \tfrac{1}{2}) + 6.55\ (v'' + \tfrac{1}{2})^2.$$

The duplicity (or multiplicity) of band heads observed by earlier writers does not appear with the low dispersion used here; so the following measurements are of the shortest wave length heads in all probability of multiple bands. Older data included but nine more prominent of these bands between λλ 5,500 and 6,900A.

TABLE 1.—*Heads of chromium oxide bands*

v', v''	Intensity	λ (I. A.)	ν (cm⁻¹) (Obs.)	ν (cm⁻¹) (Obs.−Calc.)
3, 0	0	5,356.4	18,664	−1
2, 0	3	5,564.2	17,967	2
3, 1	2	5,623.1	17,779	−2
1, 0	4	5,795.5	17,250	0
2, 1	1 L	5,852.8	17,081	0
3, 2	2	5,914.5	16,903	−6
0, 0	6	6,052.3	16,518	−1
2, 2	2	6,168.1	16,208	−2
3, 3	1	6,230.4	16,046	−5
0, 1	3	6,395.0	15,633	−2
1, 2	2	6,451.5	15,496	2
0, 2	4	6,771.8	14,763	0
1, 3	3	6,829.2	14,639	3
0, 3	2 d	7,187.1	13,910	5
1, 4	2	7,249.1	13,791	0
2, 5	1	7,313.8	13,669	−5
3, 6	0	7,375.3	13,555	0
4, 7	0	7,439.5	13,438	5
1, 5	0	7,713.9	12,960	1
2, 6	1	7,778.1	12,853	−2
3, 7	1	7,842.8	12,747	−2
4, 8	1	7,908.0	12,642	2
3, 8	1 d	8,360.3	11,958	2

L, line superposed.
d, diffuse.
Calc., calculated values obtained from formula given above.

II. VANADIUM OXIDE

The band spectrum of vanadium oxide, VO, is emitted by an arc containing vanadium, in air. The lack of data [8, 9, 10] for a more complete analysis [11] of this spectrum led to further investigation; as in the case of CrO.

The spectrum was obtained by introducing vanadium chloride into a carbon arc. Low dispersion photographs were taken, as in section I, of the visible and infra-red regions. All the bands are shaded toward longer wave lengths.

The more intense of the bands measured extend the system for which the vibrational analysis was initiated by Mecke.[12]

[8] Eder and Valenta, Atlas Typischer Spektren, Wien, 1911.
[9] Kayser u. Konen, Hanb. d. Spect., vol. 7, p. 306, 1924; for VO: H. Kayser, Handb., vol. 6, p. 786, 1912.
[10] Kiess and Meggers, B. S. Sci. Paper No. 372, 1920.
[11] Mecke, Phys. Zeit., vol. *28*, p. 514, 1927.
[12] Mecke, Phys. Zeit., vol. *28*, p. 514, 1927.

Intensity distribution among the bands is, as might be expected from the ratio of coefficients of v' and v'', a typical distribution. Duplicity (or multiplicity) of band heads, observable under high dispersion,[13] did not appear on the spectrograms, therefore the present measurements are of the shortest wave length heads in all probability of multiple bands. The new equation which represents the positions of band heads in this system, called system 1, within observational errors, is

$$\nu = 17{,}498.8 + 864.9\ (v' + \tfrac{1}{2}) - 5.70\ (v' + \tfrac{1}{2})^2 - 1{,}012.3(v'' + \tfrac{1}{2}) + 5.27(v'' + \tfrac{1}{2})^2$$

Measurements of the band heads are given in Table 2. Older data included but four of these bands: (1, 0), (0, 0), (0, 1), (0, 2).

TABLE 2.—*Vanadium oxide band heads of system 1*

v', v''	Intensity	λ (I. A.)	ν (cm^{-1}) (Obs.)	ν (cm^{-1}) (Obs.—Calc.)
4, 0	2	4, 812. 6	20, 773	2
5, 1	2 L	4, 858. 2	20, 578	1
6, 2	2 L	4, 904. 7	20, 383	1
7, 3	2	4, 951. 3	20, 191	4
3, 0	3	5, 011. 1	19, 950	−1
4, 1	4	5, 057. 3	19, 768	−1
5, 2	3 L	5, 104. 3	19, 586	0
2, 0	4	5, 228. 4	19, 121	0
3, 1	4	5, 275. 3	18, 951	1
4, 2	2	5, 323. 6	18, 779	1
1, 0	5	5, 469. 2	18, 279	0
2, 1	2	5, 516. 3	18, 123	4
0, 0	4 L	5, 737. 3	17, 425	0
2, 2	3	5, 837. 8	17, 125	−3
0, 1	4 L	6, 087. 3	16, 423	0
0, 2	2	6, 477. 8	15, 433	1
1, 3	1 L	6, 531. 6	15, 306	1
2, 4	1	6, 588. 4	15, 174	−3
0, 3	3	6, 916. 6	14, 454	3
1, 4	3	6, 974. 5	14, 334	−1
2, 5	3	7, 034. 4	14, 212	−5
3, 6	1	7, 091. 3	14, 098	−1
4, 7	0 d	7, 149. 1	13, 984	4
0, 4	1	7, 416. 9	13, 479	−2
1, 5	3	7, 474. 0	13, 376	1
2, 6	2	7, 533. 7	13, 270	2
3, 7	0 d	7, 593. 2	13, 166	5
(0, 5)	m	----------	[1] 12, 522	----------
(1, 6)	m	----------	[1] 12, 426	----------
0, 6	1 L	8, 639. 9	11, 571	−2
1, 7	1 d	8, 701. 6	11, 489	1

L, line superposed.
d, diffuse.
m, masked by strong band, 12,534.
Calc., calculated from formula, above.

[1] Calc. only.

In addition to system 1 there are 45 bands, most probably due to VO, which could not be assigned to any system. Fourteen of these

[13] Eder and Valenta, Atlas Typischer Spektren, Wien, 1911.

bands form four sequences which appear from their first differences to be related to system 1. However, no relation was found. Nor do these sequences comprise a satisfactory new system. In it there would be no band in a negative sequence if, as seems possible, the 0, +1, +2, +3 sequences be represented in the following order:

14, 503	13, 559 L	12, 629 L	11, 708 L
14, 381	13, 448	12, 534	11, 625
14, 261	13, 340		
14, 139			
14, 023 L	13, 121		
13, 899			

L, line superposed.

Additional band heads that were measured, generally of less intensity, are listed below:

20, 000	13, 629	12, 651 L
17, 288 L	13, 594 L	12, 089
17, 248 L	13, 521	12, 036
16, 831	13, 500	12, 018
15, 671	13, 431	11, 934
15, 547	13, 409	11, 661 L
14, 677 L	13, 301	11, 595 L
14, 556	12, 820 L	11, 550 L
14, 411	12, 710	11, 414
14, 291	12, 661 L	
14, 082	12, 591 L	

L, confused with line.

The writer wishes to thank the members of the spectroscopy section, especially Dr. W. F. Meggers, for kindnesses extended to him while at the Bureau of Standards.

WASHINGTON, December 22, 1931.

AIR DENSITY CORRECTIONS FOR X-RAY IONIZATION CHAMBERS

By Lauriston S. Taylor and George Singer

ABSTRACT

The international Röntgen is defined only for a given density of air (as affected by temperature and pressure). Since ionization measurements are usually carried out at other than the standard density, corrections must be made therefor. These corrections are discussed and their applications are given for (*a*) standard ionization chamber measurements, (*b*) calibration of thimble chambers against a standard, (*c*) clinical use of thimble chambers at other than the prescribed air density, (*d*) radioactive leaks for ionometer sensitivity control, and (*e*) radioactive compensators for ion current measurement.

CONTENTS

	Page
I. Introduction	385
II. Temperature and pressure corrections applied to standard ionization chambers	386
III. Temperature and pressure corrections applied to ionometers	387
IV. Application of air density corrections to calibration of an ionometer	388
V. Temperature and pressure corrections applied to radioactive ionometer controls	391
VI. Conclusions	391

I. INTRODUCTION

The unit of X-ray quantity, the Röntgen,[1, 2] has been defined by international agreement in terms of the ionization produced under stated conditions in a cubic centimeter of atmospheric air. The ionization which a given X-ray beam will produce in a given volume of air is simply proportional to the number of molecules of the air exposed to the rays; that is, proportional to the density of the air.

The density of atmospheric air depends upon the following factors: (1) Composition, (2) moisture content, (3) temperature, and (4) pressure. Air composition is extremely uniform for altitudes up to 15 km. and over the earth's surface. Ordinary variations in density resulting from change in composition do not affect the ionization produced in air. A change in temperature of 10° C. causes a change in air density due to its moisture content of only about one-half per cent. It is therefore assumed that air density changes are due entirely to variations in temperature and pressure. The density of unconfined air varies inversely as its absolute temperature and directly as its pressure. The röntgen is therefore uniquely defined when these conditions are given. To fulfill this requirement the definition states that the ionization shall be measured in air at a temperature of 0° C. and a pressure of 760 mm mercury.

[1] The quantity of radiation which, when the secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in 1 cubic centimeter of atmospheric air at 0° C. and 76 cm mercury pressure such a degree of conductivity that one electrostatic unit of charge is measured at saturation.
[2] Third International Congress of Radiology, Paris, 1931.

In formulating this definition it was not, of course, intended that ionometers should necessarily be calibrated nor that dosage measurements should necessarily be made at 0° C. and 760 mm pressure, for while not impossible, it would be extremely impractical. It was recognized that, regardless of what temperature and pressure were specified as standard, calibration and dosage measurements would be made in general under different conditions; and that this would involve temperature and pressure corrections.

Because they were of about the same order of magnitude as the error involved in the measurements, until recently, little attention has been given these corrections. Now that it is possible to make the measurements more accurately (within 0.25 per cent), these corrections can no longer be neglected. In the calibration of an ionometer there are three separate temperature and pressure corrections involved. The first is applied to the standard chamber, the second and third to the ionometer reading. These will be discussed in turn and a simplification of the process, arising from the simultaneous application of the first and second correction factors, will be noted.

II. TEMPERATURE AND PRESSURE CORRECTIONS APPLIED TO STANDARD IONIZATION CHAMBER

By the definition of the Röntgen, ionization due to "wall effects" is excluded. It is therefore to be expected that, in the open-air ionization chamber where this condition is most nearly realized, the ionization produced would vary directly as the density of the air. The density d_o at 0° C. (273°, absolute) and 760 mm mercury may be calculated from the density d_t at temperature t° C. ($273+t$, absolute) and pressure p by the equation[3]

$$d_o = d_t\left(\frac{273+t}{273}\times\frac{760}{p}\right) \quad . \tag{1}$$

Since then the ionization in the open-air chamber varies directly as the air density, number of Röntgens, r, should be given by

$$\begin{aligned} r &= I_o \\ &= I_t\left(\frac{273+t}{273}\times\frac{760}{p}\right) \\ &= I_t k \end{aligned} \tag{2}$$

Where I_t is the observed ionization per milliliter in e. s. u. at t° C. and p mm mercury and I_o is the corresponding ionization per milliliter in e. s. u. at 0° C. and 760 mm mercury.[4]

This relationship was tested experimentally first by McClung [5] in 1904 and by Crowther [6] in 1909, and found to hold within the experimental accuracy. The factor k is the air density correction which must be applied to the ionization, I_t, measured under any fixed con-

[3] This equation is an approximation good to about 0.1 per cent. The more exact expression is

$$d_o = d_t\,(1+0.00367\,t)\,\frac{760}{p}$$

[4] To distinguish between I_t and I_o in (2), Victoreen (Radiology, November, 1931, p. 1014), refers to I_o as "Röntgens reduced to zero."

[5] R. K. McClung, Phys. Zeit., vol. 5, p. 368, 1904; also, Phil. Mag., vol. 7, p. 81, 1904.

[6] J. A. Crowther, P. R. S., 1909.

ditions of temperature and pressure, in order to determine the value called for by the definition of the Röntgen. Values of k for the range of temperatures and pressures ordinarily encountered are plotted in Figure 1. This factor, therefore, enables us to determine the X-ray quantity in Röntgens under any condition, for we have simply to measure the ionization per milliliter and then multiply by k to get the ionization in e. s. u. at 0° C. and 760 mm mercury pressure. This by definition gives the X-ray quantity in Röntgens.

In the preceding discussion of the temperature-pressure correction, as applied to the standard ionization chamber, it is tacitly assumed that the electrostatic measuring system is independent of temperature and pressure. This assumption holds for all deflection systems, and for null systems involving either electrostatic compensators or hermetically sealed radioactive compensators. It does not hold for systems which are not hermetically sealed.

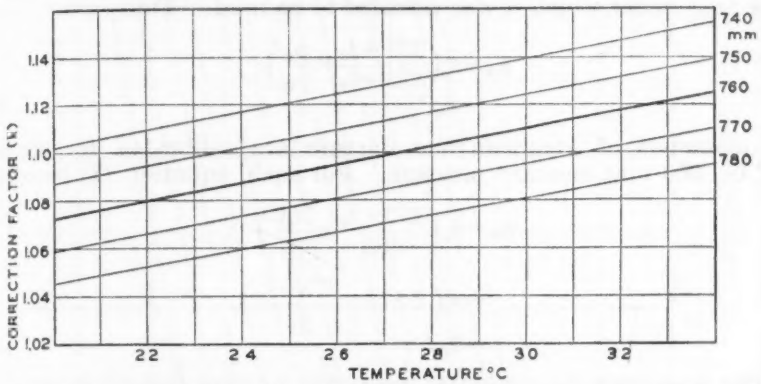


FIGURE 1.—*Correction factor to reduce ionization in e. s. u. per milliliter at a given temperature and pressure to Röntgens (e. s. u. per milliliter at 0° C. and 760 mm mercury)*

In any radioactive compensator the current is produced by air ionization which varies according to the same laws as X-ray ionization and hence is likewise subject to corrections for air density unless hermetically sealed. In the unsealed compensator the density variation is identical with that in the air ionization chamber, so that when the two are used simultaneously the air density correction experimentally vanishes. In such a case, however, it is of importance to know the air density for which the compensator calibration was made in order that the readings may be reduced by (2) to the standard density.

III. TEMPERATURE AND PRESSURE CORRECTIONS AS APPLIED TO IONOMETERS

Whether the simple air density corrections which apply for the open-air ionization chamber are also applicable to ionization chambers which are not free from "wall effects" is not known with a high degree of certainty. However, pending experimental proof, it has been universally assumed that the same corrections apply to chambers of the thimble type or others having appreciable "wall effects." The necessity for applying an air density correction when calibrating

an ionometer arises from the fact that ionometers are often used at temperatures and pressures other than those at which the calibration is made. If an ionometer receiving a given number of Röntgens (r) at known temperature (t_c) and pressure (p_c) gives a scale deflection of θ_c, it would on receiving the same number of Röntgens at some other temperature (t_w) and pressure (p_w) give another deflection (θ_w)

$$\theta_w = \theta_c\left(\frac{273+t_c}{273+t_w}\times\frac{p_w}{p_c}\right) \tag{3}$$

This correction is applied at the time of calibration of the ionometer against the standard.

Since, in general, the air density in the clinic will be variable, a second correction to be applied by the radiologist may be necessary. This is required if, at the time the ionometer is used, the temperature (t_a) and pressure (p_a) differ from the temperature (t_w) and pressure (p_w) under which it was *intended* to be used. Thus

$$\begin{aligned}\theta_w &= \theta_a\left(\frac{273+t_a}{273+t_w}\times\frac{p_w}{p_a}\right)\\ &= \theta_a c'\end{aligned} \tag{4}$$

Ionometers of American manufacture are calibrated for use at 22° C., 760 mm mercury pressure. For such, equation (4) becomes

$$\begin{aligned}\theta_w &= \theta_a\left(\frac{273+t_a}{295}\times\frac{760}{p_a}\right)\\ &= \theta_a\left(2.576\times\frac{273+t_a}{p_a}\right)\\ &= \theta_a c\end{aligned} \tag{5}$$

The correction factor in (5) (quantity in parentheses) is usually obtainable, for the range of temperature and pressure conditions ordinarily encountered, from a chart supplied by the manufacturer. It may likewise be obtained from Figure 2. Ionometers graduated to read Röntgens directly, can be correct only at the temperature and pressure at which it is intended that they be used. Under other conditions corrections must be made either by equation (4), (5), or from the chart supplied by the manufacturer.

It should be emphasized that the radiologist need make only one of the corrections discussed above and then only when high accuracy is desired. For small variations in temperature (± 3° C.) about the calibrated operating temperature (22° C.), the error introduced by neglecting the air density corrections will be only ± 1 per cent. Similarly a variation in atmospheric pressure of ± 10 mm Hg will introduce an error of about ± 1 per cent. The sum of these errors will usually lie within the experimental error of an ionometer as used clinically.

IV. APPLICATION OF AIR DENSITY CORRECTIONS TO CALIBRATION OF AN IONOMETER

Let it be required to calibrate an ionometer to measure Röntgens correctly at a temperature t_w and pressure p_w. The temperature at the time of calibration is t_c and the pressure p_c. The ionization current produced by a constant X-ray beam is first measured by

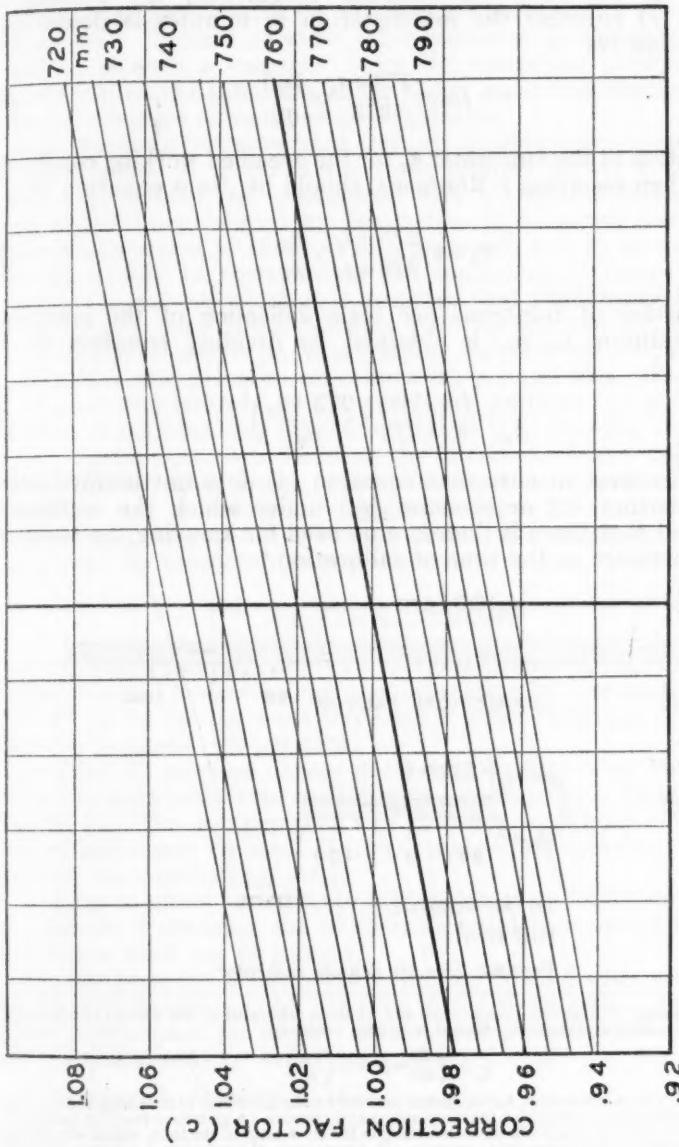


FIGURE 2.—*Correction factor (c) to be applied to an ionometer intended for use at 22° C., 760 mm mercury when used under other conditions*

means of a standard ionization chamber which indicates I e. s. u. per milliliter of air per minute. The ionometer is then placed in this beam and after m minutes shows a deflection of θ_c.

Correcting the standard chamber magnitude, the number of Röntgens (r) entering the ionometer in m minutes is determined from equation (2)

$$r = Im \times \frac{273 + t_c}{273} \times \frac{760}{p_c} \tag{6}$$

The deflection of the ionometer θ_w for the specified working conditions (t_w, p_w), when receiving r Röntgens, should be, from equation (3)

$$\theta_w = \theta_c \frac{273 + t_c}{273 + t_w} \times \frac{p_w}{p_c} \tag{7}$$

The number of Röntgens per scale deflection of the ionometer (under conditions t_w, p_w) is obtained by dividing equation (6) by equation (7)

$$\frac{r}{\theta_w} = \frac{Im}{\theta_c}\left(\frac{760}{273} \times \frac{273 + t_w}{p_w}\right)^{7} \tag{8}$$

It is of interest to note that equation (8) does not involve either the temperature (t_c) or pressure (p_c) under which the calibration is made and that there is therefore no need for knowing the temperature and pressure at the time of calibration.[8]

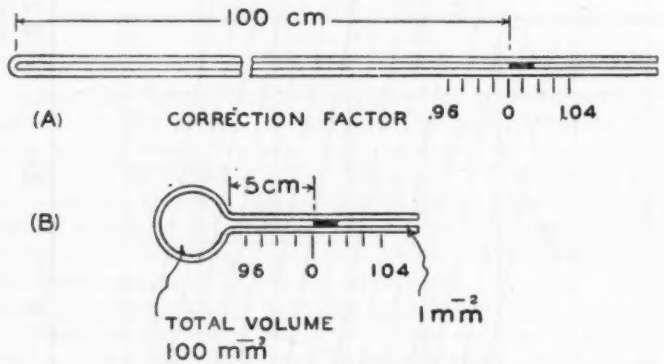


FIGURE 3.—*Air density indicator*

[7] For all ionometers of American manufacture and for those calibrated at the Bureau of Standards t_c is 22° C. and p_w is 760 mm of mercury. Equation (8) then becomes

$$\frac{r}{\theta_w} = \frac{Im}{\theta_c}\frac{295}{273} = (1.081)\left(\frac{Im}{\theta_c}\right)$$

[8] W. Nicholas, of this laboratory, has suggested and used a simple means of obtaining the air density correction without actually measuring the te—perature and pressure. A globule of mercruy in a capillary tube sealed at one end (fig. 3 (*a*)) will move according to the air density in the tube, which will, of course, vary with temperature and atmospheric pressure. If, for example, the tube has a uniform cross section and the globule is 100 cm from the sealed end, each centimeter of motion of the globule will represent about 1 per cent change in air density, giving directly the correction necessary to apply to the ionization readings. A modification of this suggestion would be to replace the long tube by a capillary and bulb of known volumes (fig. 3 (*b*)) so as to reduce the size of the apparatus. Such a device may be mounted directly on an ionometer for convenience.

V. TEMPERATURE-PRESSURE CORRECTIONS APPLIED TO RADIOACTIVE IONOMETER CONTROLS

Since ionometers are for the most part delicate instruments it is essential that some means be provided for occasionally checking their calibration. Radium or some other radioactive substance is usually provided as such a control. Since the ionization produced by the control follows the same law as for X-ray ionization similar temperature and pressure corrections are applicable.

It is therefore recommended that air density corrections on radioactive controls be made in the same manner as the corresponding corrections applied to ionometers. At the initial calibration, the scale deflection produced by the radioactive control per unit time (ratio of deflection to time) should be found, and by means of equation (3) should be corrected to the conditions of temperature and pressure (t_w, p_w) for which it is intended that the ionometer be used. When at any time the ionometer is to be checked by this control the deflection-time ratio must again be determined for existing temperature and pressure conditions (t_a, p_a) and this ratio by means of equation (4) reduced to the working conditions (t_w, p_w). By this means a check obtained from a control of this type has a real significance; a good agreement between the initial check and that obtained later (both for conditions t_w, p_w) indicating that the calibration of the ionometer has remained unchanged. Capacity controls have recently been incorporated in certain ionometers which do not require corrections for temperature or pressure.

VI. CONCLUSIONS

Of the temperature-pressure corrections discussed, that to be applied to the standard ionization chamber correcting from room temperature to 0° C., is by far the most important; under ordinary conditions it amounts to about +8 per cent.

In order to measure dosage accurately by means of an ionometer which has been calibrated in Röntgens, the following factors must be known: (1) The temperature and pressure for which it is intended that the ionometer be used, (2) the actual temperature and pressure at the time the ionometer is used.

In order to effect an accurate calibration of an ionometer by means of a standard chamber the temperature and pressure at the time of calibration need not be known.

The temperature-pressure correction to be applied to an ionometer will vary from about −2.0 per cent to +4.0 per cent. For extremes in temperature and for the low atmospheric pressures at high altitudes this correction may be as large as +7.0 per cent.

WASHINGTON, January 8, 1932.

THE ARC SPECTRUM OF PHOSPHORUS

By C. C. Kiess

ABSTRACT

For theoretical reasons phosphorus is known to have an extensive arc spectrum lying in the infra-red. Previous efforts to record this spectrum have proved unsuccessful owing to lack of sensitivity of the specially prepared photographic plates. Plates prepared by the Eastman Kodak Co. with a new infra-red sensitizer have permitted the hitherto unknown portion of the spectrum to be photographed at the Bureau of Standards. About 40 wave lengths have been measured between 9,100 and 10,800 A. These have been classified as combinations between quartet and doublet terms, which, without exception, are those required theoretically for the phosphorus atom. A survey of the entire spectrum has revealed the presence of seven new ultra-violet lines which give the connection between the doublet and quartet systems. From the series-forming terms the value of the lowest term $^4S^o_{1\frac{1}{2}}$ is found to be 90,000 cm^{-1} giving an ionization potential of 11.11 volts.

CONTENTS

	Page
I. Introduction	393
II. Experimental procedure	394
III. Results	395
1. Wave lengths and intensities	395
2. Structure of the arc spectrum	395
3. Series and ionization potential	400
4. Spectrochemical and astrophysical tests for phosphorus	400
IV. Acknowledgments	401

I. INTRODUCTION

Until recent years our knowledge of the spectrum emitted by neutral phosphorus atoms was limited to the two pairs of ultra-violet lines which Kayser[1] described as characteristic of the arc spectrum. These lines, at wave lengths 2,554.9, 2,553.3, 2,535.6, and 2,534.0 A, were also designated by de Gramont[2] as the raies ultimes of phosphorus. In 1924, however, a notable extension of the arc spectrum was made by Miss Saltmarsh[3] who observed it down to 1,671 A in the extreme ultra-violet. Her list of wave lengths begins with the characteristic group of four lines near 2,550 A and contains several other related groups which she arranged into multiplets of the doublet system.

About that time an effort was made at the Bureau of Standards to detect the deep red and infra-red lines which were suspected of being present in the arc spectrum of phosphorus. This effort was inspired by the discovery of doublet and quartet system multiplets of nitrogen[4] in the near infra-red. The spectrum of a Geissler tube containing a small amount of red phosphorus was photographed, but no lines were

[1] Handbuch der Spectroscopie, vol. 6, p. 242, 1912.
[2] Compt. rend., vol. 146, p. 1260, 1908.
[3] Phil. Mag., series 6, vol. 47, p. 874, 1924.
[4] Science, vol. 60, p. 249, 1924; vol. 61, p. 468 1925

detected in the region which could then be explored with specially sensitized photographic plates. With the advent, a few years ago, of neocyanine[5] as a sensitizing agent, a second attempt was made to get the phosphorus arc lines of long wave length, but the efforts were again fruitless. Quite recently some experimental photographic plates containing a new infra-red sensitizer were sent for test to the Bureau of Standards by Dr. C. E. K. Mees, of the Eastman Kodak Co. Phosphorus was included among the various elements whose infra-red spectra were easily recorded on these new plates. The results of this most recent attempt at extending our knowledge of the spectrum emitted by the neutral P atom are presented in this report.

II. EXPERIMENTAL PROCEDURE

The source used in these most recent experiments to obtain the phosphorus spectrum was the arc in air. For some of the observations red phosphorus was mixed with powdered graphite and the mixture packed into a cored graphite electrode. But these electrodes emitted an intense carbon band extending from 9,150 to 10,500 A, which masked all but the more intense phosphorus lines. Examination of the copper arc spectrum revealed that it has only a few lines in the region from 9,000 to 11,000 A. The graphite electrodes were, therefore, abandoned in favor of cored copper electrodes into which small rods of a P-Cu alloy were inserted. This alloy contained 30 per cent phosphorus and melted rather rapidly in the arc leaving a crater-like depression in the electrode. Into this at intervals of a minute or two small beads of red phosphorus moistened with water were inserted.

The observations of the infra-red region were made with the spectrograph carrying the concave grating ruled by Anderson with 7,500 lines per inch. This instrument has been described elsewhere.[6] To get the lines of shorter wave length, which for theoretical reasons we know must exist, a survey was then made of the entire spectrum from 2,150 A in the ultra-violet to the infra-red, using the grating with 20,000 lines per inch and the Hilger E_1 quartz spectrograph in addition to the Anderson grating. The results of this survey were the detection of seven new lines in the ultra-violet, the significance of which is pointed out below, and the demonstration of the fact that the light source employed in these observations is not adequate to bring out the fainter phosphorus lines originating in the higher energy levels of the atom.

As stated above, this investigation owes its success to the infra-red plates kindly sent to us for test purposes by Doctor Mees. The stronger phosphorus lines were recorded on them in exposures of 15 or 20 minutes. To secure the faintest lines that were measured, exposures up to two hours were required. For photographing the green, yellow, red, and near infra-red regions special plates, also supplied by Doctor Mees, were used. All the spectrograms obtained in this investigation contained exposures to the Fe or Cu arcs also, to furnish the standards required in the derivation of the phosphorus wave lengths.

[5] J. Opt. Soc. Am. & Rev. Sci. Inst., vol. 12, p. 397, 1926.
[6] B. S. Sci. Papers Nos. 312, 441, and 490.

III. RESULTS

1. WAVE LENGTHS AND INTENSITIES

The phosphorus wave lengths, which were derived from measurement of the spectrograms described above, are recorded in the first column of Table 3. Except for a few lines of intensity 0, which were measured on only one plate, all the wave lengths are the means of two to six observations and are referred to values of the Fe lines which have been adopted as secondary standards.[7] The intensities are visual estimates only. Owing to the changing spectral sensitivity of the photographic plates, the intensities recorded for groups of lines in different portions of the spectrum are not comparable with each other and are to be interpreted only as showing the relative strengths of the members of the group.

2. STRUCTURE OF THE ARC SPECTRUM

Nearly all the lines of Table 3 can be interpreted as combinations between terms, which according to atomic theory represent the different energy levels of the atom. Phosphorus, of atomic number 15, has 15 extra-nuclear electrons of which 10 fill all the allowed positions in the K and L shells, leaving 5 to be distributed among the available s, p, d orbits of the M shell. The terms arising from the various configurations assumed by these 5 valence electrons when the atom is at rest and excited are shown in Table 1. Those printed in heavy type are the ones identified in this investigation or by McLennan and McLay,[8] who, several years ago, interpreted Miss Saltmarsh's observations on the basis of the present theory of spectroscopic terms. The numerical values of the identified terms are given in Table 2. These are based on the value zero for the ground term $3p^4S_{1\frac{1}{2}}$. The metastable terms $3p^2D°$ and $3p^2P°$ are involved in the doublet system multiplets arranged by Miss Saltmarsh. The connection between these terms and those of the quartet system is supplied by the seven new lines discovered in the ultra-violet as shown in Tables 3 and 4. As indicated in Table 1 only terms with ^3P of P II as limit have been found. The relative positions of the identified terms are illustrated by Figure 1.

[7] Trans. Internat. Astron. Union, vol. 3, p. 77, 1928.
[8] Trans. Roy. Soc. Canada, series 3, vol. 21, p. 63, 1927.

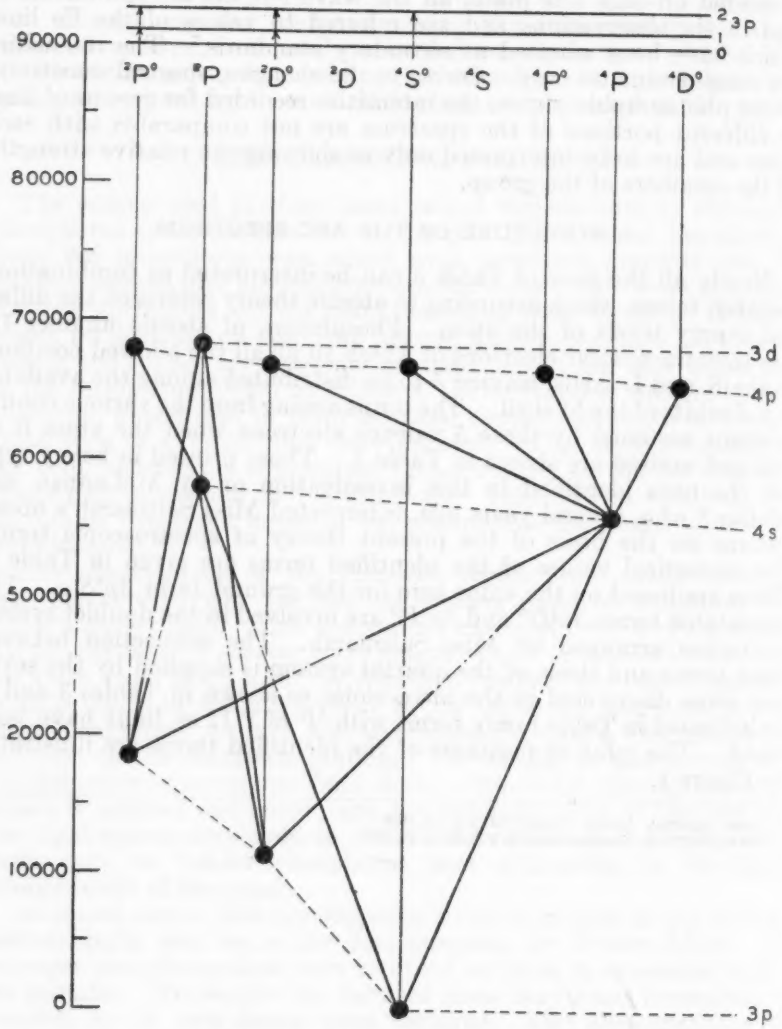


FIGURE 1.—*Term diagram of P I*

TABLE 1.—*Theoretical terms of P I*

Electron configuration	Basic term of P II		
	^3P	^1D	^1S
$3s^2.3p^3$	$^2\mathbf{P}^\circ$, $^2\mathbf{D}^\circ$, $^4\mathbf{S}^\circ$		
$3s^2.3p^2.4s$	$^2\mathbf{P}$ $^4\mathbf{P}$	^2D	^2S
$3s^2.3p^2.4p$	$^2S^\circ$, $^2\mathbf{P}^\circ$, $^2\mathbf{D}^\circ$, $^4\mathbf{S}^\circ$, $^4\mathbf{P}^\circ$, $^4\mathbf{D}^\circ$	$^2P^\circ$, $^2D^\circ$, $^2F^\circ$	$^2P^\circ$
$3s^2.3p^2.3d$	$^2\mathbf{P}$, ^2D, ^2F, ^4P, ^4D, ^4F	^2S, ^2P, ^2D, ^2F, ^2G	^2D

TABLE 2.—*Observed terms of P I*

Term type	ν	$\Delta\nu$	Series electron	Term type	ν	$\Delta\nu$	Series electron
$^4S^\circ_{1½}$	0. 0			$^4D^\circ_{0½}$	65, 378. 1	76. 6	
$^2D^\circ_{1½}$	11, 365. 8	15. 5		$^4D^\circ_{1½}$	65, 454. 7	134. 9	
$^2D^\circ_{2½}$	11, 381. 3		$3p$	$^4D^\circ_{2½}$	65, 589. 6	202. 2	
$^2P^\circ_{0½}$	18, 727. 2	25. 5		$^4D^\circ_{3½}$	65, 791. 8		
$^2P^\circ_{1½}$	18, 752. 7						
				$^4P^\circ_{0½}$	66, 347. 9	16. 8	
$^4P_{0½}$	55, 944	151		$^4P^\circ_{1½}$	66, 364. 7	183. 9	$4p$
$^4P_{1½}$	56, 095			$^4P^\circ_{2½}$	66, 548. 6		
$^4P_{2½}$	56, 344	249	$4s$	$^4S^\circ_{1½}$	66, 839. 0		
$^2P_{0½}$	57, 880. 9	297. 6					
$^2P_{1½}$	58, 178. 5			$^2D^\circ_{1½}$	66, 817. 6	57. 1	
				$^2D^\circ_{2½}$	66, 874. 7		
$^2X_{1½}$	65, 160. 9			$^2P^\circ_{0½}$	67, 975. 2	117. 2	
$^2P_{0½}$	67, 916. 2	219. 2	$3d$	$^2P^\circ_{1½}$	68, 092. 4		
$^2P_{1½}$	68, 135. 4						

TABLE 3.—*Wave lengths observed in the arc spectrum of phosphorus*

λ I. A	Intensity	Vacuum wave number	Term combinations
10, 813. 03	0	9, 245. 57	$4s^4P_{2½}$—$4p^4D^0_{3½}$
10, 681. 43	1	9, 359. 48	$4s^4P_{1½}$—$4p^4D^0_{1½}$
10, 596. 92	1	9, 434. 14	$4s^4P_{0½}$—$4p^4D^0_{0½}$
10, 581. 52	8	9, 447. 85	$4s^4P_{2½}$—$4p^4D^0_{3½}$
10, 529. 45	6	9, 494. 57	$4s^4P_{1½}$—$4p^4D^0_{2½}$
10, 511. 43	3	9, 510. 81	$4s^4P_{0½}$—$4p^4D^0_{1½}$
10, 455. 90	1	9, 561. 36	
10, 448. 48	0	9, 568. 15	
10, 432. 64	2	9, 582. 67	
10, 204. 72	2	9, 796. 71	$4s^2P_{1½}$—$4p^2P^0_{0½}$
10, 172. 01	0	9, 828. 22	
10, 146. 71	0 *b, d*?	9, 852. 72	
10, 124. 36	0	9, 874. 46	
10, 084. 22	25	9, 913. 77	$4s^2P_{1½}$—$4p^2P^0_{1½}$
9, 976. 65	5	10, 020. 66	$4s^4P_{2½}$—$4p^4P^0_{1½}$
9, 903. 74	8	10, 094. 43	$4s^2P_{0½}$—$4p^2P^0_{0½}$
9, 834. 61	1	10, 165. 39	
9, 796. 79	50	10, 204. 64	$4s^4P_{2½}$—$4p^4P^0_{2½}$
9, 790. 08	3	10, 211. 62	$4s^2P_{0½}$—$4p^2P^0_{1½}$
9, 779. 37	0	10, 222. 81	
9, 776. 90	0	10, 225. 39	
9, 760. 87	0	10, 242. 18	
9, 750. 73	25	10, 252. 83	$4s^4P_{1½}$—$4p^4P^0_{0½}$
9, 734. 74	20	10, 269. 68	$4s^4P_{1½}$—$4p^4P^0_{1½}$
9, 706. 80	1	10, 299. 23	
9, 676. 27	2	10, 331. 73	
9, 639. 06	1	10, 371. 61	
9, 608. 97	3	10, 404. 08	$4s^4P_{0½}$—$4p^4P^0_{0½}$
9, 593. 54	25	10, 420. 82	$4s^4P_{0½}$—$4p^4P^0_{1½}$
9, 563. 45	12	10, 453. 61	$4s^4P_{1½}$—$4p^4P^0_{2½}$
9, 545. 27	10	10, 473. 52	$4s^4P_{2½}$—$4p^2D^0_{1½}$
9, 525. 78	30	10, 494. 95	$4s^4P_{2½}$—$4p^4S^0_{1½}$
9, 493. 48	4	10, 530. 66	$4s^4P_{2½}$—$4p^2D^0_{2½}$
9, 452. 87	1	10, 575. 90	
9, 441. 76	3	10, 588. 35	
9, 435. 07	2	10, 595. 85	
9, 323. 55	2	10, 722. 59	$4s^4P_{1½}$—$4p^2D^0_{1½}$
9, 304. 88	3	10, 744. 10	$4s^4P_{1½}$—$4p^4S^0_{1½}$
9, 278. 82	1	10, 774. 28	
9, 193. 86	1	10, 873. 85	$4s^4P_{0½}$—$4p^2D^0_{1½}$
9, 175. 85	0	10, 895. 18	$4s^4P_{0½}$—$4p^4S^0_{1½}$
9, 153. 25	0	10, 922. 09	
2, 688. 02	2	37, 191. 08	$3p^2P^0_{1½}$—$4s^4P_{0½}$
2, 677. 12	5	37, 342. 50	$3p^2P^0_{1½}$—$4s^4P_{1½}$
2, 675. 31	1	37, 367. 76	$3p^2P^0_{0½}$—$4s^4P_{1½}$
2, 554. 93	30	39, 128. 28	$3p^2P^0_{1½}$—$4s^2P_{0½}$
2, 553. 28	40	39, 153. 57	$3p^2P^0_{0½}$—$4s^2P_{0½}$
2, 535. 65	50	39, 425. 78	$3p^2P^0_{1½}$—$4s^2P_{1½}$
2, 534. 01	25	39, 451. 29	$3p^2P^0_{0½}$—$4s^2P_{1½}$
2, 235. 77	5	44, 713. 39	$3p^3D^0_{3½}$—$4s^4P_{1½}$
2, 234. 99	3	44, 729. 00	$3p^2D^0_{1½}$—$4s^4P_{1½}$
2, 223. 35	3	44, 963. 14	$3p^3D^0_{3½}$—$4s^4P_{2½}$
2, 222. 59	0	44, 978. 52	$3p^2D^0_{1½}$—$4s^4P_{2½}$

b=broad; *d*=double.

TABLE 4.—*Multiplets from the transitions 4s→3p and 4p→4s*

Terms	$4s^3P_{0\frac{1}{2}}$ 57,880.9	297.6	$4s^3P_{1\frac{1}{2}}$ 58,178.5	2,234.5	$4s^1P_{0\frac{1}{2}}$ 55,944	151.1	$4s^1P_{1\frac{1}{2}}$ 56,095	249.0	$4s^1P_{2\frac{1}{2}}$ 56,344
$3p^4S_{1\frac{1}{2}}$			1.5		6.5		7		7
			1,719.0		1,787.5		1,782.7		1,774.8
0.0	(57,881)		58,173		55,944		56,095		56,344
$3p^4D_{3\frac{1}{2}}$			8				5		3
			2,136.79				2,235.77		2,223.35
11,381.3			46,799.2				44,713.39		44,963.14
$3p^4D_{1\frac{1}{2}}$	8		6				3		0
	2,149.81		2,136.10				2,234.99		2,222.59
11,365.8	46,515.7		46,814.2		(44,578.2)		44,729.00		44,978.52
$3p^4P_{1\frac{1}{2}}$	30		50		2		5		
	2,554.93		2,535.65		2,688.02		2,677.12		
18,752.7	39,128.28		39,425.78		37,191.08		37,342.50		(37,591.3)
$3p^4P_{0\frac{1}{2}}$	40		25				1		
	2,553.28		2,534.01				2,675.31		
18,727.2	39,153.57		39,451.29		(37,216.8)		37,367.76		
$4p^4D_{3\frac{1}{2}}$									8
									10,581.52
65,791.8									9,447.85
$4p^4D_{2\frac{1}{2}}$							5		0
							10,529.45		10,813.03
65,589.6							9,494.57		9,245.57
$4p^4D_{1\frac{1}{2}}$					3		1		
					10,511.47		10,681.43		
65,454.7					9,510.81		9,359.48		(9,110.5)
$4p^4D_{0\frac{1}{2}}$					1				
					10,596.91				
65,378.1					9,434.14		(9,283.0)		
$4p^4P_{2\frac{1}{2}}$							12		50
							9,563.45		9,796.79
66,548.6							10,453.61		10,204.64
$4p^4P_{1\frac{1}{2}}$					25		20		4
					9,593.54		9,734.74		9,976.65
66,364.7					10,420.82		10,269.68		10,020.66
$4p^4P_{0\frac{1}{2}}$					3		25		
					9,608.97		9,750.73		
66,347.9					10,404.08		10,252.83		
$4p^4S_{1\frac{1}{2}}$					0		3		30
					9,175.85		9,304.88		9,525.78
66,839.0					10,895.18		10,744.10		10,494.95
$4p^2D_{2\frac{1}{2}}$									4
									9,493.48
66,874.7							(10,779.7)		10,530.66
$4p^2D_{1\frac{1}{2}}$					1		2		10
					9,193.86		9,323.55		9,545.27
66,817.6					10,873.85		10,722.59		10,473.52
$4p^2P_{1\frac{1}{2}}$	3		25						
	9,790.08		10,084.22						
68,092.4	10,211.62		9,913.77						
$4p^2P_{0\frac{1}{2}}$	8		2						
	9,903.74		10,204.72						
67,975.2	10,094.43		9,796.71						

Among the faint lines remaining unclassified occur the differences 57.1 and 21.4, which, reference to Table 2 shows, are the separations between the terms $^4S^\circ_{1½}$, $^2D^\circ_{1½}$, and $^2D^\circ_{2½}$ coming from the $4p$ electron. It is possible to bring these lines into the classification scheme, but the new terms can not be checked from the existing wave-length data.

3. SERIES AND IONIZATION POTENTIAL

The terms from the $3p$ and $4p$ electrons form sequences from which the distances to the series limits and, consequently, the ionization potential of the atom may be found. The ground term ^3P of the first spark spectrum of phosphorus, which is the limit of the series detected in P I, has been established by Bowen [9] and is characterized by the $\Delta\nu$'s 304. 6 and 165.3. According to Hund [10] the terms $^4S^\circ_{1½}$, $^2D^\circ_{2½}$, and $^2P^\circ_{1½}$ converge to $^3P_2$, while $^2D^\circ_{1½}$ and $^2P^\circ_{½}$ converge to $^3P_1$. Applying these facts to the P I series the separations of the ground states of the arc and first spark spectra have been calculated as set forth in Table 5. The mean of the five determinations falls conveniently near 90,000 cm^{-1}, which is adopted, for the present, as the value of $3p\ ^4S^\circ_{1½}$. From this an ionization potential of 11.11 volts is derived for the neutral P atom.

TABLE 5.—*Series limits of P I*

Term	$3p\ ^4S^\circ_{1½}$	$3p\ ^2P^\circ_{½}$	$3p\ ^2P^\circ_{1½}$	$3p\ ^2D^\circ_{1½}$	$3p\ ^2D^\circ_{2½}$
Distance from limit, cm^{-1}	91, 887	71, 037	71, 158	78, 485	78, 533
Reduction to $3s^2.\ 3p^2\ ^3P_0$, P II	−470	−165	−470	−165	−470
Reduction to $3s^2.\ 3p^3\ ^4S^\circ_{1½}$, P I	0	+18, 727	+18, 753	+11, 366	+11, 381
$^4S^\circ_{1½}-{}^3P_0$	91, 417	89, 599	89, 441	89, 686	89, 444

Mean $^4S^\circ_{1½}-{}^3P_0=90{,}000\ cm^{-1}$

Ionization potential $=1.2345\times90{,}000\times10^{-4}=11.11$ v

4. SPECTROCHEMICAL AND ASTROPHYSICAL TESTS FOR PHOSPHORUS

The ultimate rays of phosphorus are given by the term combination $3p^4S^\circ-4s^4P$. These lines, lying at 1,774.8, 1,782.7, and 1,787.5 A, and classified several years ago by McLennan and McLay, fall outside the range of ordinary spectrographs and can not be relied on for making spectrochemical analyses. The group of four lines near 2,550 A, chosen by de Gramont, must continue to serve this purpose. As shown in this investigation, they originate in one of the metastable states of the atom and must be designated as penultimate lines, according to the terminology of Russell.[11]

If phosphorus is a constituent of the sun and stars its presence will be betrayed most probably by the infra-red lines resulting from the transition $4p\rightarrow4s$. The homologous element, nitrogen, is represented in the sun by only one very faint line at 8,680.4 A given by the term combination $2s\ ^4P_{2½}-2p\ ^4D^\circ_{3½}$. The corresponding line of phosphorus lies beyond the last recorded wave length in the solar

[9] Phys. Rev., vol. 29, p. 510, 1927.
[10] Linienspektren und periodisches System der Elemente, p. 184, 1927.
[11] Astrophys. J., vol. 61, p. 223, 1925.

spectrum, but the other infra-red phosphorus lines fail to show any agreement with the solar lines listed in the Revision of Rowland's Preliminary Table of Solar Spectrum Wave Lengths.[12]

IV. ACKNOWLEDGMENTS

In conclusion I wish to express my thanks to Dr. C. E. K. Mees, of the Eastman Kodak Co., for his gift of the special infra-red plates which has made possible the above investigation of the phosphorus arc spectrum; and to C. M. Saeger, jr., of the metallurgy division of the Bureau of Standards, I am also thankful for the preparation of the P-Cu alloy rods used in the electrodes. To other members of the bureau staff, notably Dr. B. H. Carroll, I am indebted for assistance rendered at various times during the course of the work.

WASHINGTON, January 25, 1932.

[12] Carnegie Institution of Washington, Publication No. 396, 1928.

SOME PHYSICAL PROPERTIES OF LEVULOSE AND ITS ESTIMATION BY COPPER REDUCTION METHODS

By Richard F. Jackson and Joseph A. Mathews

ABSTRACT

Fundamental physical properties of levulose have been determined in order to facilitate its quantitative determination. Densities of aqueous solutions are given at 20° and 25° C. for concentrations 0 to 70 per cent. Expansions have been measured over a 50° temperature interval. The density of crystalline levulose is shown to be 1.598. Refractive indices of levulose solutions have been measured at 20° and 25° C. between 0 and 90 per cent concentration. The saccharimetric rotations of levulose solutions have been measured at 20° and 25° and the change of rotation over a 50° interval of temperature determined.

Copper reduction methods for the determination of levulose have been studied. Nyns's selective method for the estimation of levulose has been modified by specifying a period of 75 minutes' digestion at 55° C. (instead of 150 minutes at 49° C.). An electrometric method for the estimation of cuprous oxide is described. The errors of analysis have been reduced by attention to details.

Simplified methods of computation have been devised which permit the rapid calculation of the levulose content of sugar mixtures.

CONTENTS

	Page
I. Introductory	404
II. Purification of levulose	404
III. Densimetric measurements	405
1. Densities of levulose solutions	405
2. Mean expansion of levulose solutions between 20° and 25°C.	408
3. Correction of Brix hydrometers for levulose solutions	410
4. Expansion of levulose solutions at wide temperature intervals	410
5. Density of crystalline levulose	411
IV. Refractive indices of levulose solutions	412
V. Saccharimetric normal weight of levulose	415
1. Measurement of saccharimetric rotation	415
2. Change of polarization of levulose between widely separated temperatures	418
VI. Copper reduction methods for total reducing sugar	419
1. Method of Munson and Walker	419
2. Lane and Eynon's volumetric method	420
VII. Biourge and Nyns's selective determination of levulose	422
1. Introductory	422
2. Effect of time and temperature upon the reduction reaction	423
3. An electrometric method for the determination of reduced copper	424
4. Standard solutions	425
5. Analytical procedure	425
6. Determination of copper-levulose equivalents	426
7. Discussion of errors	428
8. Effect of dextrose	429
9. Effect of sucrose	431
VIII. Analysis of sugar mixtures containing levulose	432
1. Introductory	432
2. Determination of levulose and dextrose in mixtures by polarization and Lane and Eynon titration. The Mathews formula	433
3. Calculation of levulose in a levulose-dextrose mixture from any method of total reducing sugar analysis and the modified Nyns method	434
4. Calculation of levulose in a levulose-dextrose mixture from Lane and Eynon titration and the modified Nyns method	434
IX. Summary	435
X. Appendix	437

I. INTRODUCTORY

The ketose sugar, levulose, or *d*-fructose, promises in the future to assume an importance in some degree commensurate with its abundance and intrinsic value. It is widely distributed in natural products in which it may occur existing in a free state, or combined with other hexoses to form compound sugars, or condensed to form polysaccharides of high molecular weight. It has been shown in a previous article[1] that crystalline levulose can be prepared from potentially abundant sources by a process capable of industrial development. Such a process requires accurate and rapid methods of analytical control. Numerous foodstuffs, many of them long-established articles of diet, contain levulose whose content has hitherto been but roughly gaged.

The accurate assay of all these materials requires a quantitative knowledge of the fundamental properties of pure levulose and its aqueous solutions. The present communication is intended to contribute data on the physical properties of levulose and on reduction methods for its estimation. While the investigation can not be considered exhaustive, each step has been carried out with the intention of meeting the needs of ordinary analytical precision.

II. PURIFICATION OF LEVULOSE

The levulose which served as the main source of supply for the experiments described in the present article had previously been prepared from the juices of the Jerusalem artichoke by hydrolysis with sulphuric acid, defecation and precipitation with lime, and crystallization from aqueous solution by the method described by Jackson, Silsbee, and Proffitt.[2] It consisted of relatively large well-formed tilted cubes and was already approximately 99.5 per cent pure. Additional supplies of levulose were derived from inulin obtained from dahlia juices. From the inulin the levulose was crystallized either directly after hydrolysis or after hydrolysis and precipitation with lime.

For further purification the sugar was dissolved in about an equal weight of water, treated with carbon, filtered, and evaporated in a vacuum to a thick sirup. The sirup was transferred to a glass jar, admixed with alcohol, seeded, and the jar tumbled end over end in a motor-driven apparatus until crystallization was complete. The crystals were purged in a centrifugal machine and thoroughly washed with alcohol. Characteristic experimental results are assembled in Table 1.

TABLE 1.—*Recrystallization of levulose from alcoholic solution*

n_D^{20} thick sirup	Levulose	Weight of sirup	Calculated weight of levulose	Strength of alcohol (by volume)	Weight of alcohol	Yield of dry crystals	
						Weight	Per cent
	Per cent	*g*	*g*	*Per cent*	*g*	*g*	
1.508	89.2	897	800	95	346	482	60
1.508	89.2	1,078	962	100	353	735	76
1.5133	91.3	359	328	95	144	211	64

[1] Jackson, Silsbee, Proffitt, B. S. Sci. Papers No. 519, vol. 20, p. 519, 1926.
[2] See footnote 1.

The method of purification was so effective that a single recrystallization of levulose, already fairly pure, produced samples which in general could not be distinguished by our measurements from those recrystallized two or three times. All samples which were used for the measurements of physical properties were recrystallized at least twice.

After a period of air drying the crystals were further dried at about 50° C. and were stored in a desiccator. Although levulose is somewhat hygroscopic, the pure crystalline substance can apparently be completely dried by simple measures. Samples prepared as described above usually contained no more than 0.02 per cent of residual moisture. Extensive experimentation showed that this could be eliminated by warming to 50° C. in a thin layer for about two hours. Such a sample was further heated at 70° C. for about 30 hours without further loss. It was then heated at 60° to 70° C. in a vacuum chamber without loss of weight. If heated to much higher temperatures the substance suffers loss of weight as a result of decomposition.[3]

III. DENSIMETRIC MEASUREMENTS

1. DENSITIES OF LEVULOSE SOLUTIONS

For a relatively short range of concentrations the densities of aqueous solutions of levulose have previously been determined by a number of investigators,[4] usually incidentally to measurements of its rotatory power. For the purpose of extending the range of concentrations and of aiding in the critical selection of valid existing data additional density measurements have been made and are reported below.

Densities were measured in the present investigation by means of flasks whose necks, 6 mm inside diameter, were graduated in 10 divisions at intervals of 0.02 ml. The volume reading could be made to one-tenth of one of these divisions thus permitting a precision of two units in the fifth decimal of density for a flask holding 100 ml. The largest of these flasks contained at the lowest graduation mark 126.333 ml at 20° C. For concentrations up to 24 per cent this flask was used exclusively. For concentrations from 30 to 60 per cent at least one measurement was made with this flask at 10 per cent intervals, while additional measurements were made with flasks containing 48.461 and 25.303 ml, respectively. The flasks were calibrated frequently at 20° and 25° C. and were found to have kept a constant volume within 0.002 ml during the course of the investigation.

The volumes of the smaller flasks could be observed with the same precision as that of the larger flask, but the percentage errors of observation became three and five times as great, respectively. It was, therefore, necessary to weight the observations in accordance with their respective accuracies. This was done by summing up the weights of levulose and of solution and the volumes of solutions which had approximately the same concentration, thus obtaining in effect one large solution for computation of data. In these averaged

[3] The conclusions respecting the drying of levulose are in harmony with previous work on this subject. For summary of previous work see Browne's Handbook of Sugar Analysis, p. 20. John Wiley & Sons, New York, 1912.

[4] Landolt u. Börnstein Tabellen, vol. 1, p. 468, 1923.

values (Table 3) the data obtained with the larger flasks predominated in proportion to their volumes.

The levulose, prepared and dried as previously described, was introduced into the weighed flask and weighed. The sugar was dissolved and the air removed from the solution by warming slightly and applying a vacuum, care being exercised to avoid loss by spattering. Water was then added to some point within the graduated scale and after mixing by a rotary motion the flask was placed in a thermostat for at least a half hour before the final observation of volume. The neck of the flask was dried by a stream of filtered air. Since the manipulation was time-consuming, mutarotation was complete before the final observation of volume.

The volumes of all solutions below 20 per cent concentration were measured at 20° and 25° C. Solutions of higher concentrations were measured at 20° and at 25° C. or at some neighboring temperature which was carefully observed.

At the time of each weighing the density of the air in the balance case was determined by weighing a glass bulb whose true mass had been determined by A. T. Pienkowsky, of this bureau. All weights were reduced to vacuum, the density of levulose being assumed 1.598 in accordance with a determination described below.

The data are assembled in Tables 2 and 3. Sylvia M. Goergen has made a least square adjustment of the data in Table 2 and computed the formulas (1) and (2).

$$D_4^{20} = 0.99823 + 0.0038893\ p + 0.0000140\ p^2 \quad (1)$$

$$D_4^{25} = 0.99708 + 0.0038557\ p + 0.0000139\ p^2 \quad (2)$$

which are valid between 0 and 20 per cent levulose.

The observed densities of the dilute solutions in Table 2 show a mean deviation from the formulas of two units in the fifth decimal for both temperatures. We, therefore, believe that the formulas are valid to some units in the fifth decimal and have solved them for 1 per cent intervals between 0 and 20 per cent levulose for purposes of tabulation. These calculated densities are given in Table 18, p. 437.

The data for the higher concentrations are given in Table 3. An adjustment was made by the method of least squares, yielding the formula,

$$D_4^{20} = 0.99936 + 0.0037842\ \mathrm{p} + 0.00001636\ p^2 \quad (3)$$

which is valid between 24 and 70 per cent. A comparison of the densities calculated from the formula with the experimental data in Table 3 discloses a mean deviation of 6 units in the fifth decimal. In our judgment the fourth decimal of the adjusted densities is reliable within about one-half a unit and we have, therefore, solved the formula between 24 and 71 per cent for 1 per cent intervals to the fourth decimal for tabulation in Table 18, p. 437. Formulas (1) and (3) yielded essentially identical values between 20 and 24 per cent.

TABLE 2.—*Densities of dilute levulose solutions at 20° and 25° C.*

TABLE 2.—*Densities of dilute levulose solutions at 20° and 25° C.*

Weight levulose (g air$_t$ brass weights)	Weight levulose (vacuum)	Weight solution (vacuum)	Concentration (vacuum)	Volume of solution t= 20.0° C.	D^{20}_4 observed	D^{20}_4 calculated formula (1) [1]	Deviation from formula (1) [1]	Volume of solution t= 25.00° C.	D^{25}_4 observed	D^{25}_4 calculated formula (2) [2]	Deviation from formula (2) [2]
g	*g*	*g*	*Per cent*	*ml*				*ml*			
3.3542	3.3561	127.463	2.633	126.377	1.00859	1.00857	+0.00002	126.532	1.00736	1.00733	+0.00003
7.2042	7.2082	128.924	5.591	126.345	1.02041	1.02041	.00000	126.509	1.01909	1.01907	+.00002
11.7513	11.7583	130.683	8.998	126.335	1.03437	1.03436	+.00001	126.521	1.03285	1.03289	−.00004
12.4818	12.4894	130.991	9.534	126.371	1.03656	1.03658	−.00002	126.550	1.03509	1.03510	−.00001
17.9369	17.9475	133.093	13.485	126.372	1.05318	1.05322	−.00004	126.557	1.05164	1.05160	+.00004
20.5601	20.5723	134.068	15.345	126.339	1.06119	1.06121	−.00002	126.540	1.05949	1.05951	−.00002
23.2543	23.2652	135.104	17.223	126.339	1.06937	1.06937	.00000	126.549	1.06759	1.06760	−.00001
23.2629	23.2767	135.100	17.229	126.328	1.06944	1.06940	+.00004				
23.3536	23.3687	135.159	17.290	126.358	1.06965	1.06966	+.00001	126.564	1.06790	1.06789	+.00001
24.3190	24.3331	135.542	17.902	126.369	1.07259	1.07257	+.00002				

[1] (1) $D^{20}_4 = 0.96823 + 0.0038893\ p + 0.0000140\ p^2$.

[2] (2) $D^{25}_4 = 0.99708 + 0.0038557\ p + 0.0000139\ p^2$.

TABLE 3.—*Densities at 20° C. of levulose solutions of higher concentrations*

Number of determinations	Weight levulose (vacuum)	Weight solution (vacuum)	Concentration	Volume solution at 20.0° C.	D_4^{20} observed	D_4^{20} calculated formula (3)[1]	Residual Obs.–Calcd.
	g	*g*	*Per cent*	*ml.*			
1	34.0572	139.282	24.452	126.418	1.10176	1.10167	+0.00009
2	61.9334	198.156	31.255	174.813	1.13353	1.13361	−.00008
3	145.2537	355.746	40.831	301.193	1.18112	1.18114	−.00002
3	173.6622	342.833	50.655	278.040	1.23303	1.23302	+.00001
2	117.1697	195.000	60.087	151.643	1.28591	1.28579	+.00012
1	23.4329	33.886	69.152	25.303	1.33921	1.33927	−.00006

[1] (3) $D_4^{20}=0.99936+0.0037842\ p+0.00001636\ p^2$.

2. MEAN EXPANSION OF LEVULOSE SOLUTIONS BETWEEN 20° AND 25° C.

By subtracting formula (1) from formula (2) and dividing by the difference in temperature we obtain formula (4), which is the mean change of density per degree between 20° and 25° C.

$$\frac{\Delta D}{\Delta t}=-(0.000231+0.00000672\ p-0.0000000224\ p^2) \qquad (4)$$

valid between 0 and 20 per cent levulose.

The solutions of concentration higher than 20 per cent were made up primarily for the determination of density at 20°, but their densities were also measured at 25° C. or some neighboring temperature which was in each case accurately observed. The data are shown in Table 4. In order to adjust these density measurements to 25° the mean change of density per degree between 20 and the temperature of observation was computed for each solution. Since the change of density with temperature is not exactly linear, it was necessary to apply a correction to the measurements of those solutions whose densities were determined at temperatures other than 25° C. This was computed by assuming that the deviation of levulose density at other temperatures was the same percentage of the mean change between 20° and 25° C. as the deviation of densities of sucrose solutions of similar concentration. This assumption was justified by the agreement shown between the corrected density coefficients of the same levulose solutions observed at different temperatures. The corrected coefficients given in column 12 of Table 4 were averaged for groups of similar concentrations in columns 13 and 14. These data were adjusted by the method of least squares yielding the formula,

$$\frac{\Delta D}{\Delta t}=-(0.0002145+0.00000795\ p-0.0000000136\ p^2) \qquad (5)$$

which is valid between 20 and 70 per cent levulose and 20° and 25° C. By application of this formula to the densities at 20° C. the data at 25° C. were computed to four decimals and are included in Table 18, p. 437.

TABLE 4.—*Density-temperature coefficient of levulose solutions of higher concentrations*

Weight levulose (air, brass weights)	Weight levulose (vacuum)	Weight solution (vacuum)	Per cent concentration (vacuum)	Temperature	Volume at $t°$ C.	D_4^t	D_4^{20} Formula (3)	Δt (t–20)	$-\Delta D$	$-\Delta D/\Delta t$	$-\Delta D/\Delta t$ Corrected to 25° C.	Averages		
												Concentration	$-\Delta D/\Delta t$ Observed	$-\Delta/\Delta t$ Formula (5) [1]
g	*g*	*g*		° *C.*	*ml*				×10⁻⁶	×10⁻⁶	×10⁻⁶	*Per cent*	×10⁻⁶	×10⁻⁶
34.0366	34.0572	138.981	24.505	25.52	126.380	1.09971	1.10193	5.52	222	402	401			
34.0366	34.0572	138.832	24.531	29.93	126.456	1.09787	1.10205	9.93	418	431	414	24.518	41	40
17.1008	17.1109	54.914	31.159	25.00	48.554	1.13099	1.13315	5.00	216	402	402			
44.7967	44.8225	142.952	31.355	29.24	126.542	1.12968	1.13410	9.24	442	478	463	31.257	43	45
60.3388	60.3746	148.764	40.584	25.71	126.407	1.17687	1.17988	5.71	301	527	525			
23.4678	23.4816	57.285	40.991	25.00	48.568	1.17948	1.18197	5.00	249	498	498			
61.3617	61.3975	149.286	41.127	25.00	126.527	1.17967	1.18266	5.00	279	558	558	40.901	53	52
15.6291	15.6383	31.150	50.202	25.00	25.373	1.22768	1.23056	5.00	288	576	576			
78.3394	78.3858	155.150	50.523	28.25	126.401	1.22744	1.23231	8.25	487	590	580	50.363	58	58
79.5899	79.6381	155.610	51.177	27.26	126.359	1.23149	1.23587	7.26	438	603	596			
79.5899	79.6381	155.606	51.179	30.67	126.576	1.22935	1.23588	10.67	653	612	594	51.178	59	59
18.7291	18.7401	32.247	58.114	25.00	25.363	1.27142	1.27453	5.00	311	622	622	58.114	62	63
98.3703	98.4296	162.390	60.613	26.60	126.418	1.28455	1.28884	6.60	429	650	645	60.613	65	65
23.4191	23.4329	33.884	69.156	25.00	25.366	1.33580	1.33929	5.00	349	698	698	69.156	70	70

[1] $(5)\frac{\Delta D}{\Delta t} = -(0.0002145 + 0.000007947\ p + 0.00000001358\ p^2)$.

The change of volume with temperature is related to the change of density with temperature by

$$\frac{dV}{dt} = -\frac{dD}{dt} \times \frac{V}{D} = -\frac{dD}{dt} \times \frac{1}{D}, \text{ since } V = 1$$

Expansion coefficients calculated from the density-temperature coefficients by this equation have been included in Table 18, p. 437.

3. CORRECTIONS TO BE APPLIED TO BRIX HYDROMETERS IMMERSED IN LEVULOSE SOLUTIONS

The densities of levulose solutions deviate appreciably from those of sucrose solutions of the same percentage composition. In order to calculate the correction at 20° C. to be applied to hydrometers which are standard for sucrose solutions at 20°, it is merely necessary to compute the "Brix" of a levulose solution of known concentration by referring its density to the sucrose density table. The departure of the percentage of sucrose found from the percentage of levulose in the given solution is the correction to be applied to the reading of a Brix hydrometer.

To determine the corrections for temperatures other than 20° C. we have available the density-temperature coefficients described in the previous section. The handbooks on cane sugar analysis [5] have, in conveniently tabulated form, the corrections to be applied to the Brix hydrometer for changes of temperature of sucrose solutions. The corrections for levulose solutions would differ from these in the ratio of the respective expansion coefficients of levulose and sucrose solutions. The mean expansion coefficients of sucrose between 20° and 25° C. were calculated from the sucrose density tables [6] and compared with the coefficients of levulose. Levulose solutions have higher expansion coefficients than sucrose solutions. At a concentration of 10 per cent the ratio of the coefficients is 1.12; at 20 per cent, 1.20; at 30 per cent, 1.22; at 40 per cent, 1.19; at 50 per cent, 1.23; at 60 per cent, 1.28; and at 70 per cent, 1.33. The corrections for sucrose were multiplied by these respective ratios to give the corrections for levulose for the change of temperature only. These corrections were then added algebraically to the corrections at 20° to give the total corrections to be applied to Brix hydrometer readings. The resulting corrections are tabulated in Table 19, p. 438.

From the data at hand it would be feasible to construct a Baumé scale of levulose densities by application of the formula [7]

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific gravity } (20°/20°)}$$

4. EXPANSION OF LEVULOSE SOLUTIONS AT WIDE TEMPERATURE INTERVALS

In the analysis of solutions containing levulose it is frequently necessary to determine polariscopic readings at widely divergent temperatures. These readings must be corrected for the expansion of

[5] For example, B. S. Circular No. 44, p. 128.
[6] Landolt u. Börnstein Tabellen, vol. 1, p. 463, 1923.
[7] Bates and Bearce, B. S. Tech. Paper No. 115.

the solution in order that both readings may be referred to the same volume concentration of solute.

A convenient volume-measuring apparatus was made by sealing a 5 ml graduated pipette to a long narrow glass bulb. This was carefully calibrated by weighing it filled with distilled water and reading the change of volume at various temperature intervals up to 100° C. The accuracy of the calibration was attested by the fact that the glass itself showed a constant cubical expansion coefficient.

For analytical methods it is convenient to use the temperature interval 20° to 70° C. As indicated in Table 5 a mean change of 0.044 ml per 100 ml per ° C. may be taken for solutions of about 5 per cent concentration and 0.045 for about 18 per cent concentration.

TABLE 5.—*Expansion of solutions between wide temperature limits*

	Concentration of solids	Temperature interval	Mean $\frac{\Delta v}{\Delta t}$ for 100 ml
	g/100 ml	*°C.*	*ml*
Pure levulose	18.4	20 – 69	0.045
	4.7	20.4– 70	.044
	3.5	20.6– 69	.043
Water		20 – 70	.042
Artichoke sample [1]		22 – 50	.038
		22 – 66.3	.042
		22 –100	.053

[1] An 80 g sample of ground fresh artichokes hydrolyzed with HCl, defecated, made to 325 ml, and filtered in preparation for analysis.

5. DENSITY OF CRYSTALLINE LEVULOSE

Since many of the calculations in the present investigation required a reduction of the weights of crystalline levulose to a vacuum, a determination of the density of the cubelike crystal form of levulose was considered necessary.[8]

For the measurement of density a flask was used of about 20 ml volume with a neck 3 mm in diameter graduated in 10 divisions of 0.0056 ml each. The volume could be observed to a precision of 0.001 ml.

Pure dry levulose was weighed in the calibrated flask, and the flask was filled with dry toluene saturated with levulose at 20° C. Air trapped in the crystals was removed by applying gentle suction while rotating the flask. The mixture was made to volume at 20.0° C. and reweighed. Three independent determinations of the density of levulose and of the toluene saturated with levulose were made. All weights were corrected to vacuum. The density ($\frac{20}{4}$) was found to be 1.598.

[8] Previously announced values: $d\ \frac{17.5}{4}$, 1.669 (crystal form not specified), Int. Critical Tables, vol. 1, p. 203, Index No. 1674; $d\ \frac{0}{4}$, 1.555 (needles), Handbook of Chemistry and Physics, Hodgman and Lange, Chem. Rubber Co., 13 ed., p. 356, 1928.

TABLE 6.—*Density of crystalline levulose*

Weight pure toluene (vacuum)	Volume toluene	D^{20}_{4} toluene	Weight levulose (vacuum)	Weight toluene (vacuum)	Total volume	Volume toluene	Volume levulose	D^{20}_{4} levulose
g	*m*		*g*	*g*	*ml*	*ml*	*ml*	
18.0143	20.794	0.86632	10.7459	12.1948	20.801	14.075	6.726	1.5977
18.0330	20.814	.86639	3.8529	15.9482	20.820	18.408	2.412	1.5974
18.0075	20.783	.86645	6.7960	14.3284	20.790	16.538	4.252	1.5984
Average		.86639						1.598

IV. REFRACTIVE INDICES OF LEVULOSE SOLUTIONS

The convenience and precision of the modern refractometer make it desirable that this instrument become available for the determination of levulose concentrations. For the measurements recorded below, three instruments were employed, namely, a Zeiss immersion refractometer, a Valentine refractometer of the Abbe type, which permitted an estimation of the fifth decimal of index, and for the highest concentrations an Abbe instrument, permitting an estimate of the fourth decimal.

The indices of solutions ranging from zero to about 20 per cent were measured by means of a Zeiss immersion refractometer. This instrument had previously been carefully calibrated at five points by L. W. Tilton, of this bureau, by means of salt solutions whose indices were determined on a precision spectrometer. It was our privilege to consult Mr. Tilton frequently during the course of these experiments and his assistance is gratefully acknowledged.

The measurements were made in a large thermostat containing about 200 liters in which temperature was maintained within 0.01° of constancy. Preliminary experiments showed that unless the temperature of the room was closely the same as that of the bath the flow of heat through the barrel of the instrument affected slightly the temperature of the small body of solution under observation. It was deemed necessary then to control the temperature of the whole refractometer as far as feasible. For the final readings the levulose solution was contained in the metal cup provided with the refractometer. The instrument itself was inserted in a large glass tube 77 mm in diameter and 28 cm long containing enough water to immerse the metal cup. The glass tube was immersed in the water of the large thermostat nearly to its upper rim and the mouth was stuffed with cotton cloth. Thermometers placed in the thermostat, in the water surrounding the cup, and in the air about the barrel of the refractometer showed essentially identical temperatures. Under these favorable conditions of temperature regulation the line of total reflection was exceedingly sharp and permitted a precision of setting within 0.1 or 0.2 of a drumhead division, or 0.01 or 0.02 of a scale division.

The instrument was illuminated by a frosted lamp placed in a large test tube immersed in the water of the thermostat, the light being reflected at the proper angle by a submerged mirror.

Concentrations of levulose were selected to coincide with the calibrated points on the scale. Before or after each determination, readings were made with distilled water. Throughout the whole

series this "zero point" remained constant at 14.42 ± 0.01 at 20.00° C. All readings were corrected to correspond to a reading of 14.50 at 20° C. or 13.25 at 25° C. for distilled water as defined by the arbitrary scale of the instrument. These readings are equivalent to indices of 1.33300 at 20.00° and of 1.33252 at 25°.

The arbitrary scale readings were translated into indices of refraction by means of the table of equivalents supplied by the manufacturer. Since the scale of the instrument had been calibrated by measurement of solutions whose indices were known, and since the instrument corrections were small, the indices of levulose solutions here presented are probably closely equivalent to absolute measurements, although admittedly they do not have the validity of measurements made with a spectrometer. It is the purpose of this bureau to undertake absolute measurements at some future time.

While the precision of setting of the line of total reflection was usually 0.01 or 0.02 scale division, corresponding to some units in the sixth decimal of refractive index, confidence is placed only in 0.1 scale division or 3 or 4 units in the fifth decimal. There are apparently some factors beside precision of setting which are as yet imperfectly controlled.

Great caution must be exercised in the use of the arbitrary scale. The data presented here refer solely to readings made on instruments graduated according to the scale as originally proposed by Pulfrich.[9] On this scale, 14.5 is equivalent to 1.33300; 50.0 to 1.34650; and 100.0 to 1.36464. If instruments are used which do not conform to the original system, the arbitrary scale readings must first be converted to refractive indices before reference is made to the index tables presented below.

In Table 7(*a*) are presented the observed data at 20° and 25° C. Sylvia M. Goergen has computed by the method of least squares interpolation formulas (6) and (7) which are valid between 0 and 20 per cent levulose, and has ascertained the agreement between the calculated and observed data.

$$n_D^{20} = 1.33300 + 0.0014159\,p + 0.00000491\,p^2 \qquad (6)$$

$$n_D^{25} = 1.33252 + 0.0014059\,p + 0.00000487\,p^2 \qquad (7)$$

The indices and scale readings at integral percentage concentrations are given in Table 20, page 438.

The measurements for the range 18 to 86 per cent levulose (Table 7(*b*)) were made with the Valentine refractometer of the Abbe type in a thermostated room maintained at 20° C. The temperature of the prisms was further controlled by water circulated from a thermostat. The readings at 25° were made in a laboratory whose temperature was uncontrolled, but the circulating water was carefully controlled at approximately 25° C. Temperature corrections resulting from deviations of the circulation water from the standard temperatures were small and could be applied with but little uncertainty.

Indices for the range 86 to 89 per cent (Table 7(*c*)) were measured with the Abbe refractometer. Both of these Abbe type refractometers had been calibrated at several scale points.

[9] Z. f. angew. Chemie, p. 1186, 1899.

All solutions were made up by weighing the pure dry levulose and adding the calculated amount of water. The supersaturated solutions were prepared by dissolving the sugar in hot water, but the final weighing was not made until the resulting solutions were cooled. All percentages are expressed in terms of weights in air with brass weights.

Least square adjustment yielded formulas

$$n_D^{20} = 1.33344 + 0.0013625\ p + 0.000006645\ p^2 \quad (8)$$

$$n_D^{25} = 1.33312 + 0.0013415\ p + 0.000006762\ p^2 \quad (9)$$

which are valid between 20 and 63 per cent levulose, and

$$n_D^{20} = 1.33377 + 0.0013570\ p + 0.000006680\ p^2 \quad (10)$$

$$n_D^{25} = 1.33345 + 0.0013360\ p + 0.000006800\ p^2 \quad (11)$$

valid between 63 and 90 per cent levulose. The experimental and calculated data are included in Table 7 and the computed indices for 1 per cent intervals in Table 20, page 438.

TABLE 7.—*Refractive indices of levulose solutions*

(a) MEASURED ON IMMERSION REFRACTOMETER

Weight levulose, air, brass weights	Weight solution, air, brass weights	Concentration of levulose	Zeiss immersion scale reading $t=20.0°$ [1]	n_D^{20} [2]	Deviation from formula (6)	Zeiss immersion scale reading $t=25.0°$ [1]	n_D^{25} [2]	Deviation from formula (7)
g	*g*	*Per cent*						
		0	14.50	1.33300	0	13.25	1.33252	0
0.4381	9.0108	4.862	32.77	1.34001	0	31.39	1.33949	+.00002
.8312	16.7541	4.961	33.15	1.34016	0			
.7440	8.8401	8.416	46.76	1.34528	+.00002			
1.5447	17.9232	8.618	47.60	1.34560	0	46.01	1.34500	0
1.9047	16.0668	11.855	60.60	1.35043	−.00005	59.02	1.34985	−.00002
1.2075	7.9699	15.151	74.66	1.35557	−.00001	72.92	1.35494	0
1.6200	8.4827	19.098	92.11	1.36185	+.00002	90.16	1.36115	0

[1] The arbitrary scale units employed here conform solely to the system as originally proposed for the immersion refractometer; thus, for example, $14.50 = n_D$ 1.33300; 100.0=1.36464. (Pulfrich, Zeit. f. angew. Chemie, p. 1186, 1899.)

[2] Derived from table of equivalents which convert arbitrary scale readings into indices of refraction.

TABLE 7.—*Refractive indices of levulose solutions*—Continued

(*b*) MEASURED ON VALENTINE-ABBE REFRACTOMETER

Weight levulose, air, brass weights	Weight solution, air, brass weights	Concentration of levulose	n_D^{20} observed	Deviation from formula (8)	n_D^{25} observed	Deviation from formula (9)
g	*g*	*Per cent*				
1.0850	5.7274	18.944	1.36157	−0.00006	1.36094	+0.00001
1.0688	4.6561	22.955	1.36822	0	1.36748	0
1.1919	4.4228	26.948	1.37503	+.00005		
1.4402	4.6590	30.912	1.38197	+.00006	1.38104	−.00001
17.1008	54.8660	31.168	1.38239	+.00003	1.38162	+.00012
44.7960	143.1180	31.300	1.38259	−.00001		
2.6925	6.5822	40.906	1.40035	+.00005	1.39932	0
23.4678	57.2366	41.001	1.40046	−.00002	1.39950	+.00001
61.3617	149.3230	41.093	1.40059	−.00006	1.39958	−.00008
15.6291	31.1260	50.212	1.41856	−.00005	1.41758	+.00005
79.5900	155.9480	51.036	1.42030	+.00001		
18.7291	32.2222	58.125	1.43510	+.00001	1.43398	+.00003
98.3700	162.6270	60.488	1.44013	−.00004	1.43894	−.00007

Weight levulose, air, brass weights	Weight solution, air, brass weights	Concentration of levulose	n_D^{20} observed	Deviation from formula (10)	n_D^{25} observed	Deviation from formula (11)
g	*g*	*Per cent*				
23.4191	33.8590	69.166	1.45964	+0.00006	1.45845	−.00005
5.8569	7.7837	75.246	1.47383	+.00013	1.47261	+.00009
8.5520	11.2766	75.838	1.47524	+.00014	1.47399	+.00008
4.8635	6.1826	78.664	1.48188	+.00003	1.48046	−.00015
4.8365	5.8752	82.321	1.49062	−.00012	1.48945	+.00001
12.0706	14.6504	82.390	1.49093	+.00002	1.48967	+.00006
4.6539	5.4159	85.930	1.49954	−.00016	1.49823	−.00001

(*c*) MEASURED ON ABBE REFRACTOMETER

5.5476	6.3893	86.826	1.5019	0		
10.2809	11.6725	88.073	1.5052	+.0001	1.5038	+0.0001
10.7568	12.1401	88.601	1.5065	+.0001	1.5051	+.0001
10.8767	12.2217	88.991	1.5073	−.0001	1.5060	0
10.9897	12.3035	89.321	1.5082	−.0001	1.5069	+.0001

V. SACCHARIMETRIC NORMAL WEIGHT OF LEVULOSE

1. MEASUREMENTS OF SACCHARIMETRIC ROTATIONS

No measurements have previously been published of the rotatory power of levulose in terms of the white light of the quartz-wedge saccharimeter. Since this instrument is the most convenient means of carrying out polariscopic analysis, the experiments here described were made to determine the normal weight of crystalline levulose (*Wo*) which in 100 ml of solution reads −100° S. and the normal weights (*W*) of aqueous solutions which, when diluted to 100 ml, show rotations in negative sugar degrees equal to their respective percentage concentrations. The distinction between *Wo* and the variable weights *W* is necessarily introduced because the rotation of levulose does not vary strictly linearly with concentration. Let it be noted that in the following discussion *Wo* alone represents the normal weight of pure crystalline levulose, while the *W*'s represent

weights of solution of pure levulose in water. The latter will yield polariscopic readings equal to their percentage concentrations.

In the absence of direct measurements it has previously been customary to assume that the normal weights of sucrose and levulose were in the inverse ratio of their respective specific rotations. This involves the assumption that the rotatory dispersions of levulose and sucrose are identical. Since the latter assumption has not been verified experimentally, and since the specific rotation itself is known with little certainty, any computed value of the normal weight is but an approximation.

The present measurements were made with a Bates type Frie saccharimeter which had been used in previous similar investigations. Its negative scale was calibrated against the quartz plates which serve as primary standards of this bureau, and whose absolute rotations have been measured many times on a high precision polarimeter. The sugar values of these plates were expressed in terms of the normal quartz plate as measured by Bates and Jackson.[10] According to this standardization the normal quartz plate rotates 40.690° for $\lambda = 5{,}461$ A, and 34.620° for $\lambda = 5{,}892.5$ A at 20° C.

The solutions whose rotations were measured were those whose concentrations and densimetric data are tabulated in Table 2. The readings were made in water-jacketed polariscope tubes whose lengths were accurately known. Temperatures were observed frequently by means of calibrated thermometers and were, in general, constant for long periods of time within 0.02° to 0.05° C. The saccharimeter was illuminated by a 100-watt lamp, the light from which passed through a 15 mm column of 6 per cent potassium dichromate before entering the instrument. Before observation the solutions usually had stood for at least two hours, and therefore, mutarotation was in every instance complete.[11]

All temperature corrections were reduced to a minimum by careful temperature control. The corrections for variations in temperature of the quartz wedges were calculated by assuming a temperature coefficient of quartz of 0.000144.[12]

In order to apply proper temperature corrections for the levulose solutions, rotations were observed at 20° and at 25° C. Since the concentrations had also been previously determined at both temperatures, this procedure served the purpose of determining the normal weights at both temperatures as well as providing a reliable means of correcting for small deviations from the two standard temperatures.

For computing the rotations, all operations and apparatus, including quartz wedges, were adjusted or corrected to the two respective standard temperatures.

The observations are recorded in Tables 8 and 9. The normal weights at the respective concentrations were computed by dividing the number of grams of levulose (c) in 100 ml $\times$ 100 by the observed rotation.

$$\frac{100 \times c}{\text{Obs. pol.}} = W \tag{12}$$

[10] B. S. Sci. Paper No. 268, vol. 13, p. 67, 1916.

[11] According to Hudson and Yanovsky (B. S. Sci. Papers No. 533, vol. 21, p. 271, 1926) the mutarotation velocity constant is 0.082 at 20° C.

[12] Bates, Bull. B. S., vol. 2, p. 245, 1906.

These values vary with concentration in the same manner as the specific rotation. The observed normal weights were correlated with the concentrations by the method of least squares, yielding the formulas

$$W_{t=20} = 18.803 - 0.01801\,c - 0.000191c^2 \quad (13)$$
$$W_{t=25} = 19.446 - 0.02061\,c - 0.000141c^2 \quad (14)$$

in which c is the number of grams of levulose in 100 ml weighed in air with brass weights.

From the adjusted normal weights the adjusted polarizations were computed by dividing each concentration by the respective adjusted normal weight. The deviations of the observed polariscopic readings from the computed readings are shown in columns 6 of Tables 8 and 9.

The normal weight of the normal solution or the concentration of levulose required to read exactly $-100°$ S. was calculated from formulas (13) and (14) by imposing the condition that $c = Wo$.[13] Upon solution of the resulting equations we obtain 18.4067 g for the normal weight (Wo) of levulose at 20°, and 19.0030 g at 25° C. We shall accept the values 18.407 and 19.003, respectively, weighed in air with brass weights.

TABLE 8.—*Saccharimetric rotations of levulose solutions at 20° C.*

Levulose (vacuum)	Weight levulose in 100 ml (air, brass weights)	D_4^{20}	Observed polarization at 20° C. ×(−1)	Calculated polarization ×(−1)	Deviation obs.−calc. polarization ×(−1)	Observed normal weight	Calculated normal weight formula (13)
Per cent	*g*		°*S*	°*S*	°*S*	*g*	*g*
5.5909	5.7018	1.02041	30.49	30.50	−0.01	18.701	18.694
8.9977	9.3017	1.03437	49.98	49.96	+.02	18.611	18.619
9.5341	9.8771	1.03656	53.11	53.09	+.02	18.597	18.606
13.4846	14.1916	1.05318	76.63	76.59	+.04	18.519	18.509
15.3442	16.2737	1.06119	88.11	88.16	−.05	18.471	18.459
17.222	18.4063	1.06937	100.02	100.00	+.02	18.404	18.407
17.229	18.4146	1.06944	100.01	99.96	+.05	18.397	18.406
17.289	18.4821	1.06965	100.44	100.46	−.02	18.400	18.405
	18.5672		100.87	100.89	−.02	18.406	18.403
17.952	19.2444	1.07259	104.66	104.67	−.01	18.388	18.385

TABLE 9.—*Saccharimetric rotations of levulose solutions at 25° C.*

Levulose (vacuum)	Weight levulose in 100 ml (air, brass weights)	D_4^{25}	Observed polarization at 25° C. × (−1)	Calculated polarization ×(−1)	Deviation obs.−calc. polarization ×(−1)	Observed normal weight	Calculated normal weight formula (14)
Per cent	*g*		°*S.*	°*S.*	°*S.*	*g*	*g*
5.5909	5.6944	1.01909	29.47	29.47	0.00	19.321	19.324
8.9977	9.2880	1.03285	48.28	48.27	+.01	19.249	19.242
13.4846	14.1709	1.05165	74.12	74.09	+.03	19.118	19.125
15.3442	16.2479	1.05949	85.18	85.19	−.01	19.075	19.074
17.2218	18.3758	1.06759	96.56	96.62	−.06	19.031	19.019
17.229	18.3834	1.06762	96.69	96.66	+.03	19.014	19.019
17.289	18.4520	1.06790	97.06	97.03	+.03	19.012	19.017
17.952	19.2104		101.12	101.12	.00	18.998	18.998

[13] This yields the equations

$$c_{t=20} = 18.803 - 0.01801\,c - 0.000191\,c^2$$
$$c_{t=25} = 19.446 - 0.02061\,c - 0.000141\,c^2$$

The c^2 terms were determined numerically with sufficient accuracy by interpolation between two calculated values for solutions approximately normal.

If the polarization were to indicate directly the percentage of levulose in the sample taken for analysis, it would be necessary to take a different normal weight for each concentration. It is more convenient to employ a constant normal weight and apply corrections for the deviations of rotation from constant proportionality. To determine these corrections, formulas (13) and (14) were solved for each integral value of c from 1 to 20 g yielding the respective normal weights. Each value of c multiplied by 100 and divided by its respective normal weight yields a numerical value equal to the actual rotation for each concentration. But each value of c divided by the constant normal weights 18.407 and 19.003 yields the percentage of levulose in the sample taken for analysis. The deviation of the actual rotation from the percentage of levulose is a measure of the correction to be applied to the polarization in order to give the true percentage composition of the sample. These corrections are given in Table 21, page 439.

2. CHANGE OF POLARIZATION OF LEVULOSE BETWEEN WIDELY SEPARATED TEMPERATURES

The high temperature coefficient of the rotatory power of levulose suggests that polariscopic readings at widely separated temperatures may serve as a measure of the concentration of the sugar.[14] The measurement is in a high degree dependent upon the efficiency of the apparatus used for temperature control. The measurements reported below were made in water-jacketed continuous polariscope tubes, 400 mm in length, constructed of Monel metal. Within the water jacket was placed a spiral baffle which imparted a rotary motion to the water stream, thus greatly increasing the velocity of water over the surface of the tube. We acknowledge gratefully the assistance of M. J. Proffitt and J. A. Bogan in the designing of these tubes.

Water was supplied by centrifugal pumps operating in thermostats held at the high and low temperatures, respectively. The temperatures of polarization were observed by means of thermometers placed in the circulating water immediately before its entrance into and after its emergence from the water jacket. In general, the water stream was so abundant and rapid that the two thermometers showed closely agreeing temperatures. The mean of the readings of the two thermometers was assumed to be the true temperature of the solution. The stem corrections of the thermometers were carefully calculated for the high temperature observation.

The observations for concentrations of levulose from 3 to 9 g in 100 ml were made in a 400 mm Bates-Fric saccharimeter. The remaining measurements were made in a Schmidt and Haensch 600 mm instrument with a quartz plate of $+100.05°$ sugar value placed in series with the tubes.

Corrections were made for the deviation of the temperature of the quartz wedges and the quartz plate from the standard temperatures. We suggest as a matter of definition that the high temperature polarization be measured with the quartz wedges at the same temperature as that of the low temperature measurement. The expansion of the solution at the high temperature was corrected for by using the expansion coefficients given in Table 5.

[14] For a review of this subject see Browne's Handbook of Sugar Analysis, p. 297, 1912, John Wiley & Sons, New York.

The experimental data shown in Table 10 indicate that between room temperature and about 70° to 75° C. 1 g of levulose in 100 ml changes 0.0344° S. for each degree change in temperature. Contrary to Vosburgh's[15] conclusions, our data show no systematic deviation of the coefficient with concentration of sugar. The measurements indicate that levulose can be determined by this method with a mean precision of about one-third of 1 per cent of the quantity measured. This degree of precision has, however, been secured only by great attention to detail and by averaging a considerable number of observations.

TABLE 10.—*Change of polarization of levulose between wide temperature intervals*

Weight levulose in 100 ml at 20° C.	Number of observations	Polarization[1] at $t°_1$ C.	Temperature $t°_1$ C.	Polarization[1] at t_2	Temperature $t_2°$ C.	ΔP	ΔT	$\frac{\Delta P}{\Delta T \times g}$	Levulose calculated	Error
g		°*S.*		°*S.*		°*S.*	°*C.*		*g*	*Per cent*
3.000	7	15.94	20.10	10.84	69.54	5.10	49.44	0.03439	2.998	−0.07
6.000	8	32.21	19.59	21.56	70.95	10.65	51.36	.03456	6.026	+.43
9.000	6	48.46	19.70	32.39	71.78	16.07	52.08	.03428	8.967	−.41
12.000	3	62.90	24.13	41.77	74.83	21.13	50.70	.03473	12.111	+.93
15.000	3	78.78	24.13	52.57	75.16	26.21	51.03	.03424	14.927	−.52
18.000	3	95.02	24.00	63.12	75.70	31.90	51.70	.03428	17.934	−.35
Average.								.03441		.35

[1] Polarizations are corrected for length of tube and temperature of quartz wedges.

VI. COPPER REDUCTION METHODS FOR TOTAL REDUCING SUGAR

1. METHOD OF MUNSON AND WALKER

The method of Munson and Walker[16] is well adapted to the determination of total reducing sugar over a wide range of concentrations. In the articles in which the method was originally described the authors gave the copper equivalents for dextrose and invert sugar but no equivalents for levulose. In order that this widely employed method might become available for sugar mixtures having a high ratio of levulose, we have made analyses of pure levulose for the purpose of determining the respective copper equivalents.

The details[17] of the analyses were carried out rigorously in accordance with Munson and Walker's specifications, except that copper was determined by thiosulphate titration instead of by direct weighing of the copper precipitate. The titration method is less tedious and eliminates many of the uncertainties inherent in gravimetric analysis.

Immediately preceding the analysis of each levulose solution a similar analysis was conducted with a standard dextrose solution of such sugar content that both precipitated approximately the same weight of copper.

In Table 11 are shown the data obtained. Columns 2 and 3 show that the present experiments are in essential agreement with Munson and Walker's data on dextrose. Column 6 shows the weight of levulose (calculated from columns 4 and 5) which yields the same weight of copper (column 2) as the dextrose in column 1, and column 7 the ratio of weights of the sugars. These observed ratios were plotted against the weight of dextrose and from the smoothed curve the values in column 8 were read. The reciprocals of these values are given in column 11.

[15] J. Am. Chem. Soc., vol. 42, p. 1696, 1920.
[16] J. Am. Chem. Soc., vol. 28, p. 663, 1906; vol. 29, p. 541, 1907; vol. 34, p. 202, 1912.
[17] Quoted paragraphs are reprinted from the Report on Chemical Methods for Reducing Sugars, by R. F. Jackson, associate referee (J. Assoc. Official Agri. Chem., vol. 13, p. 199, 1930).

From column 8 it is apparent that the reducing ratio is a function of the concentration of sugar. Evidently the practice of employing a single-valued ratio, regardless of concentration of sugar, is hazardous, unless it has been demonstrated that the ratio is constant.

In column 10 are the ratios of weights of invert sugar to dextrose computed from Munson and Walker's table. If it is assumed that the reducing power of a sugar mixture is an additive property of the constituents, the ratios of invert sugar to dextrose can be extrapolated to those of levulose to dextrose, as is done in column 9. A comparison of these extrapolated with the experimental ratios (column 8) reveals a serious discrepancy. Either the rule of mixtures is inaccurate or some error exists in the experimental data. Such error may occur either in the present data for levulose or in Munson and Walker's values for invert sugar.

TABLE 11.—*Copper-reducing equivalents of dextrose and levulose by Munson and Walker's method*

Weight dextrose taken	Copper found	Copper from Munson and Walker's table	Weight levulose taken	Copper found	Weight levulose yielding same copper as dextrose	Ratio of weights of levulose to dextrose observed	Ratio from curve	Munson and Walker's table extrapolated to levulose	Ratio: Weights of invert sugar to dextrose (Munson and Walker)	Reducing power of levulose (reciprocal) of column 8
1	2	3	4	5	6	7	8	9	10	11
mg	*mg*	*mg*	*mg*	*mg*	*mg*					
200	375.1	374.7	213.1	374.9	213.1	1.066	1.067	1.056	1.028	0.937
200	375.9	374.7	212.5	374.1	213.5	1.068	1.067	1.056	1.028	.937
160	307.0	306.8	170.5	303.1	172.7	1.079	1.075	1.060	1.030	.930
120	234.6	235.4	127.9	231.0	129.8	1.082	1.082	1.065	1.033	.924
100	197.7	198.3	106.6	194.4	108.4	1.084	1.086	1.067	1.034	.921
85.75	173.0	171.5	94.03	173.6	93.7	1.093	1.089	1.070	1.035	.918
64.31	129.9	130.2	70.52	130.8	70.0	1.089	1.093	1.074	1.037	.915
42.88	88.8	87.9	47.01	88.8	47.0	1.097	1.097	1.079	1.040	.912

2. LANE AND EYNON'S VOLUMETRIC METHOD

More expeditious and in most instances more precise than the gravimetric estimation of total reducing sugar is the volumetric method of Lane and Eynon.[18] The method is described in the references cited and may be used without modification for the analysis of sugar mixtures containing levulose.

In their tabulation of empirical factors Lane and Eynon give the values for dextrose, invert sugar, and levulose. Inasmuch as levulose in natural products is almost invariably accompanied by dextrose in widely varying ratio, it has been found desirable to tabulate factors interpolated at 10 per cent intervals between pure dextrose and pure levulose. The interpolated factors are given in Table 22, page 439.

The degree of precision attainable by this method is to a considerable extent dependent upon the skill and experience of the analyst. As a corollary of this fact individual procedure and possible variations in the composition of the reagents may cause variations in the standard factors. It is therefore important that the analyst standardize his own analysis by titrating pure solutions of the respective sugars, thus ascertaining the correction to be applied to Lane and Eynon's tables. The correction can be applied uniformly to the tabulated factors or to the burette reading.

[18] J. Soc. Chem. Ind., vol. 42, p. 32, 1923. J. Assoc. Official Agri. Chem., vol. 9, p. 35, 1926.

The calculation of levulose in a levulose-dextrose mixture determined by methods to be described below is necessarily based upon the uncorrected factors interpolated from Lane and Eynon's data. For this purpose it is necessary to compute what the burette reading would be if Lane and Eynon's factors applied to the titration without correction. The correction to the burette reading (for 25 ml of Soxhlet reagent) is most conveniently determined by reference to the last three columns of Table 22, page 439.

The method of derivation of the quantities in this table is as follows: The factor correction found as described above by titrating 25 ml of Soxhlet solution with a standard reducing sugar solution is

$$c = \frac{S\,T}{100} - F \tag{15}$$

in which c = factor correction (difference between determined and tabulated factors), S = mg of reducing sugar per 100 ml in solution taken, T = observed titration, and F = factor in Lane and Eynon's table corresponding to the observed titration. Lane and Eynon's factors satisfy the equation

$$F_0 = (119.36 + 0.0471\ T_0 + 7.3\ R) \tag{16}$$

where T_0 = titration in ml and R = ratio of levulose to total reducing sugar. The factor for any titration is

$$F_1 = 119.36 + 0.0471\ T_1 + 7.3\ R + c$$

where c is the factor correction from equation (15). Since

$$100\frac{F}{T} = \text{mg sugar}$$

$$100\frac{F_0}{T_0} = 100\frac{F_1}{T_1}$$

or

$$\frac{119.36 + 0.0471\ T_0 + 7.3\ R}{T_0} = \frac{119.36 + 0.0471\ T_1 + 7.3R + c}{T_1}$$

hence

$$T_1 - T_0 = \frac{cT_0}{119.36 + 7.3\ R} \tag{17}$$

To solve equation (17) we must know the ratio of levulose to total reducing sugar as well as the titer and factor correction. Since in an unknown solution we do not know the ratio, R, and as T_0 will differ from T_1 by a very small amount, we can write as an approximation

$$T_1 - T_0 = \frac{cT_1}{119.36 + (7.3 \times 0.50)} = \frac{cT_1}{123.0} \tag{18}$$

in which we assume that the ratio is 0.50. The introduction of the approximation influences the value of the correction by a negligible amount, as the following example shows.

Assume that the observed titration of a pure levulose solution was 25.00 ml and the factor correction was 2.0. From equation (18) we obtain

$$T_1 - T_0 = 0.41 \text{ ml}$$

and

$$T_0 = 24.59 \text{ ml}$$

whereas from the more rigorous equation (17)

$$T_0 = 24.61 \text{ ml}$$

The difference between the two calculated values is within the experimental error of the titration.

The corrections in Table 22 were calculated from equation (18). It should be noted that when the factor correction, c, is positive, the titer correction is to be subtracted from the observed titer and vice versa.

VII. BIOURGE AND NYNS'S SELECTIVE DETERMINATION OF LEVULOSE

1. INTRODUCTORY

In an effort to distinguish between levulose and dextrose by reduction methods Biourge [19] made the important observation that at 50° C. the quantity of copper reduced in Ost's reagent by levulose was ten times as great as that reduced by dextrose. At a later period Nyns [20] elaborated the principle and determined the copper-levulose equivalents for a wide range of sugar concentrations. Notwithstanding Biourge's observation that dextrose had an appreciable reducing action under the conditions of the analysis, Nyns stated that neither dextrose nor other hexoses reduced even traces of copper. In a preliminary study of the method Jackson [21] found that dextrose exerted a reducing action equivalent to about one-thirteenth of the reducing power of levulose. This ratio appeared to be constant regardless of the relative concentrations of levulose and dextrose.

Important contributions to the method have been made by Zerban and Sattler [22] and by Schuette and Terrill.[23]

Nyns's method proved extremely serviceable for the estimation of levulose in numerous products. For immediate purposes it was used in unmodified form, but the long period of digestion (2½ hours) made it tedious and time consuming. In order to render the method more convenient and reliable we suggest the modifications described below which permit a shorter time of digestion, an accurate and rapid method of copper determination, occasional agitation during reduction, and higher concentrations of copper sulphate (25.3 g) [24] in Ost's reagent. The agitation of the solution during reduction was

[19] Bull. assoc. école sup. brasserie Louvain, January, 1898.
[20] Sucr. Belge, vol. 44, p. 210, 1924. Bull. assoc. école brasserie Louvain, vol. 25, p. 63, 1925. C. A., vol. 19, p. 1236, 1925.
[21] J. Assoc. Official Agri. Chem., vol. 9, p. 178, 1926.
[22] Ind. Eng. Chem., vol. 2, p. 307, 1930.
[23] J. Am. Chem. Soc., vol. 52, p. 4960, 1930.
Although the articles by Zerban and Sattler, and Schuette and Terrill, have a direct bearing on the present article, lack of available space prevents a detailed discussion of their conclusions.
[24] Nyns specified 15 g of copper sulphate. For a discussion of the concentration of copper see article by Zerban and Sattler, footnote 22.

suggested by Zerban and Sattler in order to obviate the unequal distribution of copper, an occurrence which we also had observed in analyzing samples of high levulose concentration.

2. EFFECT OF TIME AND TEMPERATURE UPON THE REDUCTION REACTION

In an effort to shorten the 2½-hour period of digestion specified by Nyns the reduction was carried out at various temperatures, the amount of copper reduced being determined at appropriate intervals of time. Parallel experiments were conducted in which the samples contained either pure levulose or levulose admixed with known weights of dextrose. The temperatures selected were 48.6°, 54.8°, and 58.8° C. The experimental results are shown diagrammatically in Figure 1. The reduction occurs relatively rapidly in the early stages

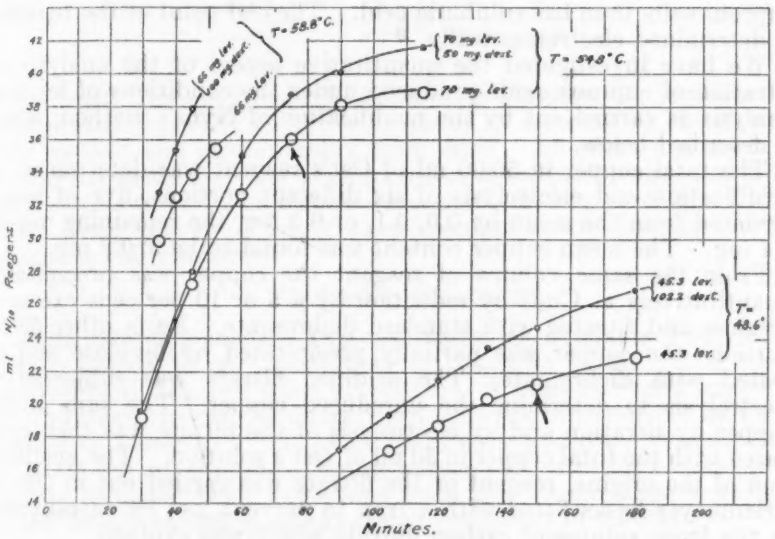


FIGURE 1.—*Rate of reduction of copper in Ost's solution by levulose at various temperatures*

of the reaction and continues more slowly for an indefinite period. The terminal point of 2½ hours selected by Nyns is evidently arbitrary and does not represent a definite end point. The filtrate from the reduced copper continues to reduce more copper even upon standing at room temperature.

The curves at 54.8° and even at 58.8° show a retardation in the rate of precipitation in the later stages of the reaction and permit the arbitrary selection of a terminal point. For the reduction at 54.8° the reaction approaches completion in about 75 minutes, or one-half the time specified by Nyns. This period was deemed sufficiently convenient for regular operation, and moreover, the reducing effect of dextrose was found to be about one-thirteenth of that of levulose, as had proved to be the case with Nyns's original method. For further investigation, therefore, the temperature of 55° C. and the time of 75 minutes were selected.

3. AN ELECTROMETRIC METHOD FOR THE DETERMINATION OF REDUCED COPPER

In Nyns's process for the selective determination of levulose the most tedious or most uncertain step has in the authors' experience been the determination of reduced copper. The most expeditious method is the permanganate titration process originally devised by Mohr and adopted by Nyns for his method. The permanganate method has in practice proved less reliable and convenient than theoretical considerations would lead one to expect and has, in general, had but limited application.

A priori considerations led to the belief that if potassium dichromate could be substituted for permanganate the defects inherent in processes which required the use of the latter reagent could be eliminated. Of greatest importance for the present purposes it permits the use of hydrochloric acid which has a greater solvent effect on cuprous salts than has sulphuric acid. The end point of the titration is determined electrometrically. [25]

We have investigated the quantitative aspect of the analysis by titration of cuprous oxide produced under the conditions of levulose analysis as carried out by the modification of Nyns's method, which is described below.

The total copper in 50.00 ml of Ost's reagent was determined by acidification and electrolysis of six different portions, five of which deviated from the mean by 0.0, 0.1, or 0.2 mg, the remaining one by 0.4 mg. The mean copper content was found to be 320.2 mg.

From the same volume of reagent the copper was precipitated quantitatively as Cu_2O by reduction by a 5 or 10 per cent excess of levulose and titrated with standard dichromate. From other 50 ml portions the copper was partially precipitated by levulose and titrated with dichromate. The acidified filtrate was subjected to electrolysis to determine the unreduced copper. The sum of the copper by titration and by electrolysis of the filtrate was then compared with the total copper in 50 ml of Ost's solution. The acidification of the original reagent or the filtrate was carried out in 500 ml Erlenmeyer flasks fitted with a trap to prevent loss by entrainment in the large volume of carbon dioxide which was evolved.

Electrolysis was carried out in a volume of about 200 ml containing 3 ml of sulphuric acid and 1.5 ml of nitric acid in excess of the acid required to neutralize the carbonate. Copper was deposited on platinum gauze electrodes by a current of about 0.18 ampere flowing for a period of about 17 hours. The absence of copper from the electrolyzed solutions and from the completely reduced Ost's solutions was assured by the absence of discoloration after addition of hydrogen sulphide. Experimental results are shown in Table 12.

[25] G. S. Forbes and E. P. Bartlett, J. Am. Chem. Soc., vol. 35, p. 1527, 1913.

TABLE 12.—*Determinations of reduced copper in 50 ml of Ost's solution by electrometric dichromate titration*

[Total copper taken, 320.2 mg. 1 ml of dichromate equals 10 mg of copper]

Dichromate 0.1573 *N*	Cu in filtrate	Cu recovered	Deviation	Error
ml	*mg*	*mg*	*mg*	*Per cent*
32.06	0	320.6	+0.4	+0.13
32.01	0	320.1	−.1	−.03
32.05	0	320.5	+.3	+.09
32.05	0	320.5	+.3	+.09
32.04	0	320.4	+.2	+.06
32.03	0	320.3	+.1	+.03
32.01	0	320.1	−.1	−.03
30.18	18.1	319.9	−.3	−.09
30.23	17.9	320.2	0	0
30.32	17.1	320.3	+.1	+.03
27.18	48.2	320.0	−.2	−.06
23.43	85.9	320.2	0	0
Average	.....	320.26	±0.17	±0.05

Evidently the electrometric dichromate titration of cuprous oxide precipitated from Ost's solution is about as accurate as the electrolytic method and incomparably more rapid. An effort was made to extend the method to the determination of copper precipitated from Soxhlet's solution. The results were, however, less satisfactory than those cited above. Further experimentation will be required to determine its reliability.

4. STANDARD SOLUTIONS

Potassium dichromate.—This substance is available from commercial sources in very pure form. A quantity of the "C. P." salt was recrystallized and dried at 150° C. A standard solution, $N\times$-0.15730 was prepared by dissolving 7.7135 g of the purified salt and making to 1 liter at 22° C. One ml of such a solution is equivalent to 10.00 mg of copper. During subsequent titrations changes of volume resulting from deviations from this temperature were corrected for by assuming an expansion coefficient of 0.00020.

Ferrous ammonium sulphate.—A solution, $N\times0.1573$, was prepared by dissolving 61.8 g of the commercial C. P. hexahydrate, adding 5 ml of concentrated H_2SO_4 and making to 1 liter. This solution lost about 0.3 per cent of its reducing power per day. The practice during the present investigation was to titrate it against the dichromate solution at the beginning and at the end of each series of analyses. During the few hours lapse of time no appreciable change was observable.

Ost's solution.—Dissolve 250 g of K_2CO_3 (anhydrous) in about 700 ml of hot water and add 100 g of pulverized $KHCO_3$. Agitate until completely dissolved. Cool and add with very vigorous agitation a solution of 25.3 g of pure $CuSO_4.5H_2O$ in 100 to 150 ml of water. Make to 1 liter and filter.

5. ANALYTICAL PROCEDURE

Transfer 50 ml of Ost's reagent to a 150 ml Erlenmeyer flask and add by means of an accurately graduated pipette a volume of the solution to be analyzed which contains not more than 92 mg of

levulose or its equivalent of a levulose-dextrose mixture, remembering that dextrose has about one-twelfth of the reducing power of levulose. Add enough water to make the total volume 70 ml. Immerse in a water bath regulated preferably within 0.1° C. at 55° C. Digest for exactly 75 minutes, agitating with a rotary motion at intervals of 10 or 15 minutes.

At the expiration of the prescribed time filter the precipitated copper on a closely packed Gooch crucible and wash flask and filter thoroughly without attempting to transfer the precipitate quantitatively. It is well, however, to transfer all of the loose-lying cuprous oxide, leaving in the flask only the small portion which adheres to the walls. Remove the asbestos mat by means of a glass rod and transfer to a 400 ml beaker. Add 5 or 10 ml of water and disintegrate the asbestos mat. Add a carefully measured volume of standard potassium dichromate ($N \times 0.1573$) in excess of the volume required to oxidize the cuprous oxide. In many cases the expected amount of precipitated copper will be roughly known and it will be possible to gage the volume of dichromate which will supply a 3 to 4 ml excess. If the amount of precipitated copper is not even roughly known it is preferable to add an amount which will supply an assured excess, since a very large excess introduces no uncertainty, provided its volume is accurately measured. Of this volume about 1 ml is added to the original reaction flask in order that the residual cuprous oxide may be dissolved and subsequently added to the remainder of the solution. Add to the Erlenmeyer flask by means of a graduated cylinder about 50 ml of 1:1 HCl. Pour slowly into the 400 ml beaker with constant stirring and continue to stir until the cuprous oxide is completely dissolved. Wash the Erlenmeyer with a jet from the wash bottle, receiving the rinsings in the beaker. Examine the asbestos critically by looking through the bottom of the beaker, which is held above the eye. If any undissolved cuprous oxide remains it can be clearly discerned as dark-colored particles. Immerse the crucible in the acidified solution to dissolve such cuprous oxide as remained in it. Remove the crucible with a glass rod, washing it free from solution. Dilute the solution as thus prepared to about 250 ml and titrate the excess of dichromate with ferrous sulphate electrometrically.

If a large number of samples require analysis the solutions may for convenience be allowed to await the titration after the addition of dichromate and hydrochloric acid.

6. DETERMINATION OF COPPER-LEVULOSE EQUIVALENTS

On each of six days a series of analyses was made to determine the copper reduced by varying amounts of levulose. The samples were introduced into the water bath at intervals of six or seven minutes. At the time each sample was immersed or removed all those previously introduced were momentarily agitated by a rotary motion to insure the uniform distribution of cupric copper. At the expiration of 75 minutes the solutions were filtered, washed, and prepared for titration by one worker, while the other performed the titration and prepared additional samples for analysis. By proceeding in this manner we were enabled to perform conveniently about 25 analyses in a period of about four hours. An analyst working alone can perform about 17 analyses in the same period of time.

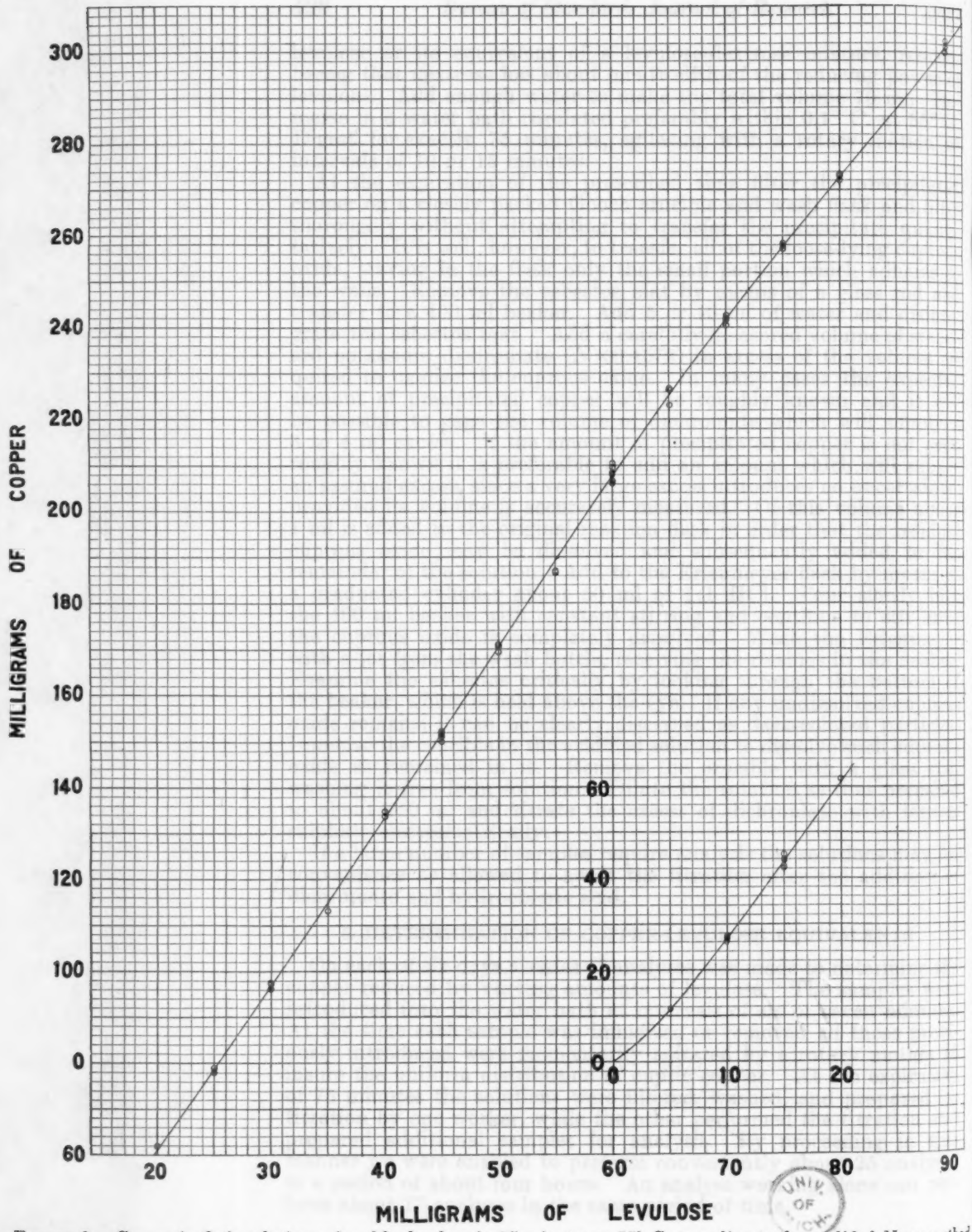


FIGURE 2.—*Copper in Ost's solution reduced by levulose in 75 minutes at 55° C. according to the modified Nyns method*

99675-32. (Face p. 427.)

The experimental results are assembled in Table 13 and plotted in Figure 2. The experiments were arranged in such a manner as to show the reproducibility of duplicate experiments performed, on the same day, on different days, and after an extended period of time. Three different preparations of Ost's solution were used for the analyses. One solution was used on March 26, 1931, and preserved for the final series on April 28 in order to be assured that no change in results occurred after an extended period of aging.

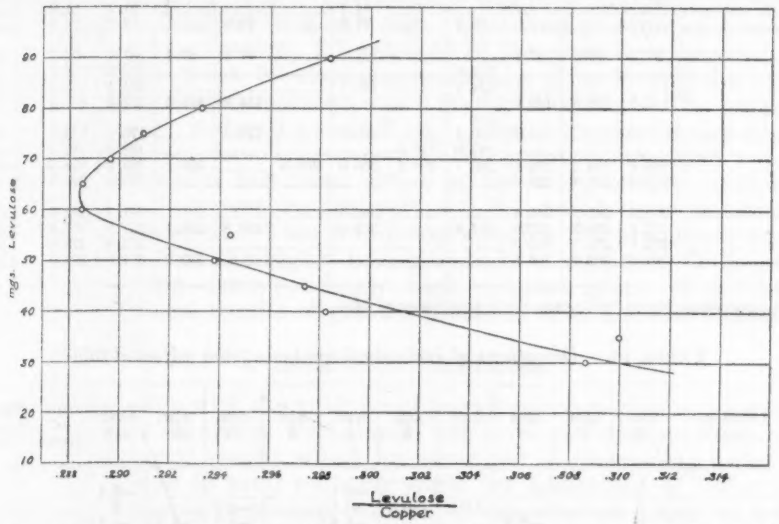


FIGURE 3.—*Showing the variation of the levulose-to-copper ratio with varied concentrations of levulose*

The averaged values of the copper precipitated by each quantity of levulose are given in column 11. The weights of levulose divided by the respective weights of copper yielded the factors which were serviceable for conversion of copper into its levulose equivalent. These factors are plotted as a function of copper in Figure 3.

Preliminary calculations made to adjust the experimental data by the method of least squares failed to yield an equation which represented the data accurately. The adjustment was accordingly made by drawing Figure 3 on a large scale. In determining the curve the points were weighted according to the number of determinations included in each average. The equivalents for integral weights of copper are tabulated in Table 23, page 440.

TABLE 13.—*Copper-levulose equivalents*

[Milligrams of copper reduced by varying amounts of levulose]

Levulose (mg)	Mar. 26	Mar. 27	Mar. 31	Apr. 3	Apr. 3	Apr. 8	Apr. 8	Apr. 28	Apr. 28 [1]	Average	Adjusted	Ratio: Levulose / Copper
5						11.6				11.6	11.7	4.310
10				27.3	27.0	26.1		26.6		26.7	26.7	3.738
15	43.7		44.0			42.1		42.6	45.4	43.6	43.7	3.444
20						61.7				61.7	61.0	3.242
25				78.0		77.8		78.9		78.2	78.7	3.197
30	97.2	96.1	97.4					97.2	97.4	97.1	96.7	3.086
35				112.9						112.9	114.7	3.100
40				134.7		133.5				134.1	132.5	2.983
45	152.3	151.8	149.9					151.0	151.5	151.3	151.0	2.974
50				170.4		169.3		170.8		170.2	170.0	2.938
55				187.0	186.6					186.8	189.3	2.944
60	209.6	208.2	210.6	206.7	206.1	208.0	208.0		206.6	208.0	208.0	2.885
65	223.0	226.4	226.6							225.3	225.3	2.885
70	242.0	242.6	241.6			240.4				241.7	242.0	2.896
75	257.7	258.3	257.9	257.8		257.2		257.8	258.1	257.8	257.8	2.909
80	272.1	27o.1	273.3							272.8	273.0	2.933
90	301.5	302.7	300.1						302.2	301.6	301.5	2.984

[1] Analyses performed with same Ost's solution as on Mar. 26.

TABLE 14.—*Deviations of individual analyses from adjusted table*

Levulose (mg)	Mar. 26	Mar. 27	Mar. 31	Apr. 3	Apr. 3	Apr. 8	Apr. 8	Apr. 28	Apr. 28 [1]	Average	Sum of errors	Mean deviation
5						−0.1				−0.1		
10				+0.6	+0.3	−.6		−0.1		0		
15	0		+0.3			−1.6		−1.1	+1.7	−.1		
20						+.7				+.7		
25				−.7		−.9		+.2		−.5	+6.2	
30	+0.5	−0.6	+.7					+.5	+.7	−.6	−5.7	0.63
35				−1.8						−1.8		
40				+2.2		+1.0				+1.6		
45	+1.3	+.8	−1.1						+.5	+.3		
50				+.4		−.7		+.8		+.2		
55				−2.3	−2.7					−2.5	+11.4	
60	+1.6	+.2	+2.6	−1.3	−1.9	0	0		−1.4	0	−13.2	1.2
65	−2.3	+1.1	+1.3							0		
70	0	+.6	−.4			−1.6				−.3		
75	0	+.5	+.1	0		−.5		0	+.4	0		
80	−.9	+.1	+.3							−.2	+6.3	
90	0	+1.2	−1.4						+.7	+.1	−7.1	.6

[1] Analyses performed with same Ost's solution as on Mar. 26.

7. DISCUSSION OF ERRORS

In Table 14 are shown the deviations of the individual analyses from the adjusted table of equivalents. For convenience of critical study these experiments have been divided into three groups representing, respectively, high, medium, and low concentrations of levulose. The essential agreement of positive with negative residuals in each group shows that the adjusted table represents fairly the experimental data. For the whole series the average deviation of a single experiment is 0.8 mg of copper. In the group of high levulose concentrations (65 to 90 mg) the mean error of a single determination is 0.6 mg of copper. The average weight of copper reduced in this group of analyses was

273 mg. The mean error of analysis was therefore but 0.2 per cent of the quantity measured.

In the median range of levulose concentrations (35 to 60 mg) the average deviation from the adjusted copper equivalents is 1.2 mg of copper. This error is twice as great as that in either of the two other groups. The reason for this is not far to seek, for an inspection of Figure 3 shows that this is the region of greatest curvature of the levulose-copper ratio, and relatively large variations occur with slight alterations of conditions. The average weight of copper reduced in this group of analyses was 176 mg. The average error of a single experiment was, therefore, 0.7 per cent of the quantity measured.

In the range of low levulose concentrations (5 to 30 mg) the mean error of a single determination was 0.63 mg of copper. The average weight of copper reduced was 58.8 mg. The average error of a single analysis was, therefore, 1.1 per cent of the quantity measured.

In recapitulation the mean errors in the high, median, and low groups of analyses were, respectively, 0.2, 0.7, and 1.1 per cent of the quantities measured. This result corroborates the prediction made by Jackson [26] that the higher concentrations of copper in Ost's solution, permitting correspondingly high concentrations of levulose, yielded analytical results of greater precision than the Ost's reagent used by Nyns.

8. EFFECT OF DEXTROSE

In conjunction with the analyses of pure levulose solutions described above similar analyses were made on levulose-dextrose mixtures. The experimental results which are arranged in descending order of ratio of levulose to total reducing sugar are assembled in Table 15. The total copper precipitated (column 4) was converted into its levulose equivalent by reference to Table 23, page 440. The result is designated in column 5 of Table 15, "apparent levulose." The difference between apparent levulose and the true levulose taken represents in terms of milligrams of levulose the reducing effect of the weight of dextrose taken. The quotient of the weight of dextrose divided by the excess of apparent over the true levulose is the number of milligrams of dextrose which is equivalent in reducing power to 1 mg of levulose. These values are given in column 6 of Table 15 and also in Table 16, which permits a more discriminating analysis of the results. It is at once apparent from Table 16 that even for extreme variations of levulose and dextrose concentrations no considerable systematic deviations from a constant dextrose equivalent of levulose occur. The experiments include a range of ratios of levulose to total reducing sugar (column 1 of Table 15) varying from 2.9 to 75 per cent. No attempt was made to determine the reducing action of dextrose for mixtures of higher levulose ratio, since for such mixtures the total effect of dextrose amounts to a very small correction, and any probable deviation from a constant reducing power would be negligible.

[26] J. Assoc. Official Agri. Chem., vol. 13, p. 200, 1930.

TABLE 15.—*Reduction of levulose–dextrose mixtures*

[Modified Nyns method]

Ratio: Levulose / Total sugar	Levulose taken	Dextrose taken	Copper precipitated	Apparent levulose found	Mg Dextrose ⌒ 1 mg levulose	Dextrose taken +12.4	Corrected levulose found [1]	Error of levulose taken
Per cent	*mg*	*mg*	*mg*	*mg*		*mg*	*mg*	*Per cent*
100.0	75	0	257.8	75.0				
75.0	75	25	264.9	77.4	10.4	2.0	75.4	+0.5
75.0	50	16.7	174.7	51.3	12.8	1.35	49.95	−.1
61.6	80	50	284.3	83.9	12.8	4.0	79.9	−.1
58.4	70	50	255.6	74.3	11.6	4.1	70.2	+.3
54.5	60	50	223.7	64.5	11.1	4.1	60.4	+.7
50.0	75	75	276.3	81.1	12.3	6.1	75.0	0
50.0	50	50	184.6	53.8	12.8	4.0	49.8	−.2
47.4	45	50	164.7	48.7	13.5	4.0	44.7	−.7
45.5	25	30	87.6	27.5	12.0	2.4	25.1	+.4
44.2	80	100	295.2	87.7	13.0	8.1	79.6	−.5
41.2	70	100	268.0	78.4	11.9	8.1	70.3	+.4
Mean error								0.35
37.5	60	100	240.3	69.5	10.5	8.1	61.4	+2.3
37.5	30	50	113.0	34.6	10.9	4.05	30.55	+1.8
33.3	75	150	293.6	87.1	12.3	12.1	75.0	0
31.0	45	100	179.9	52.6	13.1	8.1	44.5	−1.1
25.0	50	150	211.3	61.0	13.7	12.1	48.9	−2.2
25.0	25	75	99.3	30.9	13.3	6.1	24.8	−.6
23.1	30	100	126.5	38.3	12.0	8.1	30.2	−.7
23.1	15	50	59.6	19.6	10.9	4.1	15.5	+3.3
16.7	60	300	286.3	84.5	12.2	24.25	60.25	+.4
15.4	50	275	244.9	71.0	13.1	22.2	48.8	−2.4
Mean error								1.5
13.0	15	100	74.9	24.0	11.1	8.1	15.9	+6.0
10.4	40	350	225.0	64.9	14.0	28.3	36.7	−8.2
9.8	30	275	180.8	52.8	12.1	22.2	30.6	+2.0
8.3	45	500	282.9	83.4	13.0	40.4	43.4	−3.6
5.7	30	500	238.1	68.8	12.9	40.4	28.4	−5.3
4.8	25	500	207.7	60.0	14.3	40.4	19.6	−21.6
2.9	15	500	178.7	52.3	13.4	40.4	11.9	−20.6
Mean error								9.8

[1] Column 5 minus column 7.

The mean of all the values given in Table 16 is 12.4. The most generally useful part of the table will be that which is applicable to samples whose compositions lie in the lower left quadrant bounded by levulose, 45 to 80 mg, and dextrose, to 150 mg. Such samples may range from 20 to 100 per cent in ratio of levulose to total reducing sugar. Within this quadrant the mean value for the reducing action of dextrose is 12.3 in essential agreement with the average of all determinations made. If we take the upper left-hand quadrant bounded by levulose, 15 to 50 mg, and dextrose, to 150 mg (overlapping the quadrant previously considered), the mean value is 12.3. The upper right-hand quadrant bounded by levulose, 15 to 50 mg, and dextrose, 250 to 500 mg, has the mean value 13.1.

TABLE 16.—*Reducing action of dextrose by the modified Nyns method*

[Tabulated figures indicate the number of milligrams of dextrose which is equivalent in reducing power to 1 mg of levulose]

Dextrose / Levulose	16.7	25	30	50	75	100	150	250	275	300	350	500
15				10.9		11.0						13.4
25			12.0		13.3							14.3
30				10.9		12.0			12.0			12.9
40											14.0	
45				13.5		13.7						13.0
50	12.8			12.8			13.7		13.1			
60				11.1		10.5				12.2		
70				11.6		11.9		13.2				
75		10.4			12.3		12.3					
80				12.8		13.0						

Viewed as a whole the data in Table 16 seem to indicate that for constant amounts of dextrose, its reducing effect is practically independent of the concentration of levulose. For greatly increased concentrations of dextrose (for example, 350 to 500 mg) its reducing power seems to decrease slightly. The most disturbing feature is the variability of individual analyses. These variations will, however, seriously affect the precision of the levulose analysis only when the dextrose content of the sample is relatively high.

In order to ascertain the degree of precision which may be expected in the analysis of levulose-dextrose mixtures, we have divided Table 15 into three sections, in each of which the mean error of analysis has been computed. The first group of analyses indicates that sugar mixtures ranging from 40 to 100 per cent levulose can be analyzed with a mean error of about 0.35 per cent, which is but slightly greater than the error of analysis of pure levulose solutions. Samples ranging from about 15 to 40 per cent ratio of levulose to total sugar can be analyzed with a mean error of about 1.5 per cent.

Below a 15 per cent ratio the dextrose corrections become very large, and the errors of analysis increase greatly. Even within this range, however, the analytical results have some significance. One could, for example, determine the ratio of levulose to total sugar within one-half of 1 unit. For such low ratios of levulose it is probable that a direct determination of dextrose [27] would yield more reliable results.

9. EFFECT OF SUCROSE

A limited number of analyses were made of levulose-sucrose mixtures in order that the modified method described above might be available for the determination of levulose in the products of the cane-sugar industry. In harmony with the conclusions of Zerban and Sattler we find that the effect of sucrose is small. The analytical results are given in Table 17. The weight of copper precipitated by sucrose in the presence of levulose can be represented by the formula:

$$\text{mg Cu} = 3.32\,S - 0.31\,S^2 + 0.27 \qquad (19)$$

in which S is the number of grams of sucrose. The equation is valid only between 1 and 5 g of sucrose.

[27] Kline and Acree, B. S. Jour. Research, vol. 5 (RP247), p. 1063, 1930.

TABLE 17.—*Reducing effect of sucrose in the presence of levulose by the modified Nyns method*

Levulose	Sucrose	Copper precipitated	Copper [1] precipitated by levulose	Copper precipitated by sucrose	Average	Calculated copper [2]
mg	*g*	*mg*	*mg*	*mg*	*mg*	
10	1	30.5	26.7	3.8		
25	1	82.1	78.7	3.4	3.3	3.3
50	1	172.6	170.0	2.6		
75	1	261.1	257.8	3.3		
50	2	177.2	170.0	7.2	5.65	5.65
75	2	261.9	257.8	4.1		
10	5	35.3	26.7	8.6		
25	5	87.8	78.7	9.1	9.0	9.0
50	5	179.3	170.0	9.3		
0	5	2.4				

CALCULATED COPPER PRECIPITATED BY INTEGRAL WEIGHTS OF SUCROSE [1]

Sucrose.....g..	1	2	3	4	5
Copper.....mg..	3.3	5.7	7.4	8.5	9.0

[1] From Table 23, p. 440.
[2] Cu (mg) = 3.32 S − 0.31 S^2 + 0.27.

VIII. ANALYSIS OF SUGAR MIXTURES CONTAINING LEVULOSE

1. INTRODUCTORY

There are six general methods of analysis from which it is theoretically possible to select three in order to determine the three quantities—total solids, levulose, and dextrose. If, in addition, sucrose is present a Clerget analysis must be performed. Aside from the Clerget analysis the methods to be considered are: (1) Total dry substance by density, refractive index, or desiccation; (2) total reducing sugar by Lane and Eynon titration or other method; (3) Nyns's levulose analysis; (4) aldose by the method of Kline and Acree; (5) direct polarization; and (6) levulose by temperature coefficient.

It is well known that desiccation processes for the determination of total solids are difficult if the sample contains levulose. The difficulty is greatly increased when levulose becomes the predominating substance. We have, therefore, in the early sections of the present article given particular attention to the determination by densimetric and refractometric methods. While these methods yield only apparent dry substance it is probable that the values (especially those derived from refractive index) will be more serviceable than those derived from desiccation methods.

From a mixture containing no optically active or reducing substance but levulose and dextrose, a combination of any two of the methods 2 to 6 (except the combination 3 and 6) will yield a complete sugar analysis. In the presence of other optically active substances only combinations 2 and 3, 2 and 4, and 3 and 4 will yield correct results. Combinations 2 and 3, and 2 and 5 will be considered in detail. Other combinations, and in particular the question of purity determination, will be discussed in subsequent articles.

2. DETERMINATION OF LEVULOSE AND DEXTROSE IN MIXTURES BY POLARIZATION AND LANE AND EYNON TITRATION. THE MATHEWS FORMULA

This combination of analytical processes and the method of calculation described below are valid under the assumptions that the only optically active or reducing substances present in the sample are dextrose and levulose and that the rotation of a sugar mixture is the algebraic sum of the rotations of the constituents whose specific rotations are referred to the concentration of total sugar rather than to the partial concentration of each.[28] The calculations below are also based upon the assumption that the titrations are made with reagents and procedure to which Lane and Eynon's factors apply without correction. If necessary, the burette readings should be corrected in the manner described on p. 439 (Table 22).

While the method of determination applies strictly only to pure mixtures of levulose and dextrose, it may sometimes be applied to crude mixtures to yield a proximate analysis by neglecting the errors due to optically active impurities. If the sample in question has previously been subjected to acid hydrolysis the error introduced in the analysis of plant juices is usually small.

For a constant ratio of levulose to total reducing sugar the polarization (P) will vary with the concentration of total sugar, while the titration (T) will vary inversely as the concentration. Since for the reducing sugar analysis we usually must dilute the sample, the product, $P \times T$, will vary with the dilution (D), but the product, $\frac{P \times T}{D}$, will vary but slightly with dilution. It is therefore possible to tabulate in a brief space the ratios of levulose to total sugar as functions of the quantities $\frac{P \times T}{D}$ and T. The tabulation is given in Table 24, page 442.

For convenience this method of solution will be referred to in subsequent articles as the Mathews formula.[29]

The rotation of any mixture in saccharimeter degrees at 20° C. is given by

$$P_{(t=20°)} = -[5.31154 + 0.0064928(x+y)]x + [3.03537 + 0.0020837(x+y)]y, \quad (20)$$

where x and y are the concentrations of levulose and dextrose, respectively, in grams per 100 ml.

The total reducing sugar, S, as determined by Lane and Eynon's method is given by

$$S = \frac{100F}{T} \quad (21)$$

T is the titer in ml and is corrected to correspond to the factor F (see p. 421). F is given approximately by the relation

$$F = 119.36 + 0.0471\ T + 7.3\ R \quad (16)$$

where $R = \frac{x}{x+y}$.

[28] Vosburgh, J. Am. Chem. Soc., vol. 43, p. 219, 1921.
[29] This ingenious method of calculation was devised by the junior author. (R. F. J.)

S in equation (21) is related to the total reducing sugar by

$$DS=x+y \tag{22}$$

where D is the number of volumes to which one volume of the solution polarized is diluted for the Lane and Eynon titration.

In constructing Table 24, page 442, the quantity $\frac{P\times T}{D}$ was computed for selected values of T, D, and R from equations (20), (21), and (22). Since $\frac{P\times T}{D}$ is not exactly linear with RD as varies, a small correction, $c=\frac{f\times D}{T}$, must be applied in which f is a factor given in a supplementary table. An example illustrating the operation of the table is given on page 440.

3. CALCULATION OF LEVULOSE IN A LEVULOSE-DEXTROSE MIXTURE FROM ANY METHOD OF TOTAL REDUCING SUGAR ANALYSIS AND THE MODIFIED NYNS'S METHOD

If a sample has been analyzed for total reducing sugar by any selected method and for levulose by the modification of Nyns's method described above, the resulting data are sufficient for a calculation of levulose and dextrose by a general method of successive approximations. Compute from the reducing sugar analysis the total reducing sugar in a given volume or weight expressed as dextrose, unless the approximate composition of the sample is known. In the latter case refer the copper to the sugar mixture of that composition. From the Nyns's analysis compute the apparent levulose in the same volume or weight of sample. Subtract the apparent levulose from the total sugar to obtain the apparent dextrose. Divide the apparent dextrose by 12.4 and subtract the quotient from the apparent levulose to obtain a new approximation to the levulose content. Subtract the approximate levulose from the total sugar to obtain a truer value for the dextrose, again divide by 12.4, continue the approximation in the same manner until successive calculations show a negligible change in the levulose. For a final calculation the copper reduced in the total sugar analysis must be referred to the sugar mixture of the finally determined composition.

If the sample under examination contains sucrose which has been determined by Clerget analysis the copper precipitated in the Nyns's analysis is first corrected for the sucrose by Table 17 before the method of approximations is applied.

If the total sugar is determined by Lane and Eynon titration and levulose by the modified Nyns's method the tedious calculation described above can be avoided by the method described below.

4. CALCULATION OF LEVULOSE IN A LEVULOSE-DEXTROSE MIXTURE FROM LANE AND EYNON TITRATION AND THE MODIFIED NYNS'S METHOD

In order to avoid the tedious procedure described in the previous paragraph a convenient method of solution was devised applicable when reducing sugar is determined by Lane and Eynon's method.

Lane and Eynon's factors for levulose-dextrose mixtures (Table 22, p. 439) may be expressed by

$$F = 119.36 + 0.0471\ T + 7.3\ R \tag{16}$$

in which F is the factor, T the titer, and R the ratio of levulose to total reducing sugar. The total reducing sugar (S) in a sample is

$$\frac{100\ F}{T} = S \tag{21}$$

whence

$$100\ \frac{119.36 + 0.0471\ T + 7.3\ R}{T} = S \tag{23}$$

The true levulose is

$$L = SR$$

and the apparent levulose is

$$\begin{aligned} l &= L + 0.0808\ S(1-R) \\ &= 0.9192\ SR + 0.0808\ S \end{aligned}$$

whence

$$S = \frac{l}{0.9192\ R + 0.0808} \tag{24}$$

Combining equations (23) and (24)

$$\frac{T \times l}{100} = (119.36 + 0.0471\ T + 7.3\ R)\ (0.9192\ R + 0.0808) \tag{25}$$

Equation (25) was solved for varying R and T and plotted in a series of curves in each of which T was constant. These curves were found to be very nearly straight lines, and even for widely varying values of T were but slightly displaced from each other. It was, therefore, possible to tabulate a complete series of values of R for relatively few values of T. In solving the analytical data it is merely necessary to multiply the burette reading for the Lane and Eynon titration by the milligrams of apparent levulose in 100 ml and refer the product divided by 100 to Table 25, page 444. Under the proper titration, T (or interpolated between two adjacent columns), the ratio of levulose to total sugar is read directly. An example showing the method of operation is given on page 444.

IX. SUMMARY

1. The densities of aqueous levulose solutions are expressed by

$$D_4^{20} = 0.99823 + 0.0038893\ p + 0.0000140\ p^2$$
$$D_4^{25} = 0.99708 + 0.0038557\ p + 0.0000139\ p^2$$

which are valid between 0 and 20 per cent

$$D_4^{20} = 0.99936 + 0.0037842\ p + 0.0000164\ p^2$$

valid between 20 and 70 per cent.

2. The mean expansion coefficient between 20° and 25° C. is

$$\frac{\Delta D}{\Delta t} = -(0.000231 + 0.00000672\ p + 0.0000000224\ p^2)$$

valid between 0 and 20 per cent, and

$$\frac{\Delta D}{\Delta t} = -(0.0002145 + 0.00000795\ p + 0.0000000136\ p^2)$$

valid between 20 and 70 per cent.

3. Corrections to convert the readings of Brix hydrometers standard for sucrose solutions to percentage of levulose have been computed and tabulated.

4. The density of crystalline levulose $\left(\frac{20°}{4°}\right)$ has been found to be 1.598.

5. Refractive indices of levulose solutions are represented by the formulas:

$$n_D^{20} = 1.33300 + 0.0014159\ p + 0.00000491\ p^2$$

$$n_D^{25} = 1.33252 + 0.0014059\ p + 0.00000487\ p^2$$

which are valid between 0 and 20 per cent levulose, and

$$n_D^{20} = 1.33344 + 0.0013625\ p + 0.000006645\ p^2$$

$$n_D^{25} = 1.33312 + 0.0013415\ p + 0.000006762\ p^2$$

which are valid between 20 and 63 per cent levulose, and

$$n_D^{20} = 1.33377 + 0.0013570\ p + 0.000006680\ p^2$$

$$n_D^{25} = 1.33345 + 0.0013360\ p + 0.000006800\ p^2$$

valid between 63 and 90 per cent levulose.

6. The saccharimetric normal weight of crystalline levulose is 18.407 at 20° C. and 19.003 at 25° C.

7. The normal weights of dilute solutions are represented by

$$W_{(t=20)} = 18.803 - 0.01801\ c - 0.000191\ c^2$$

$$W_{(t=25)} = 19.446 - 0.02061\ c - 0.000141\ c^2$$

in which c = grams of levulose in 100 ml.

8. A table of concentration corrections for constant normal weights has been computed.

9. For the temperature interval 20° to 70° C. each gram of levulose in 100 ml decreases 0.0344° S in rotation for each degree rise in temperature. This value appears to be independent of concentration of sugar.

10. Determinations of the copper reduced by levulose in Munson and Walker's method have been made. It is shown that the ratios of the reducing powers of dextrose to levulose are not constant, but are a function of concentration of sugar.

11. A modification of the Nyns selective reduction method for levulose has been suggested which permits a performance of the analysis in about one-half the time previously specified.

12. An accurate and rapid electrometric method of cuprous-oxide analysis by dichromate titration is described.

13. The copper reduced by pure levulose by the modified Nyns method has been determined and tabulated.

14. The reducing power of dextrose has been found to be essentially independent of the concentration of dextrose or levulose, 12.4 mg of dextrose being equivalent in reducing power to 1 mg of levulose under the conditions prescribed for the modified Nyns's method.

15. The reducing effect of sucrose has been found to be

$$mg\ Cu = 3.32\ S - 0.31\ S^2 + 0.27$$

in which S is the number of grams of sucrose. The formula is valid only between 1 and 5 g of sucrose.

16. Methods of calculation of the concentration of levulose in samples analyzed by optical and chemical methods are described.

X. APPENDIX

TABLE 18.—*Densities of levulose solutions and mean density and expansion coefficients between 20° and 25° C.*

[All weights corrected to vacuum]

Levulose	D_4^{20}	D_4^{25}	$\frac{-\Delta D}{\Delta t}$	$\frac{\Delta v}{\Delta t}$	Levulose	D_4^{20}	D_4^{25}	$\frac{-\Delta D}{\Delta t}$	$\frac{\Delta v}{\Delta t}$
Per cent			$\times 10^{-6}$	$\times 10^{-6}$	*Per cent*			$\times 10^{-6}$	$\times 10^{-6}$
0	0.99823	0.99708	231	231	35	1.1568	1.1544	48	42
1	1.00214	1.00095	238	237	37	1.1618	1.1593	49	42
2	1.00607	1.00484	245	243	38	1.1668	1.1643	50	43
3	1.01003	1.00877	252	249	39	1.1718	1.1693	50	43
4	1.01402	1.01272	259	255	40	1.1769	1.17435	51	43
5	1.01803	1.01670	266	261	41	1.1820	1.1794	52	44
6	1.02207	1.02071	273	267	42	1.1872	1.1845	53	44
7	1.02614	1.02475	280	273	43	1.1923	1.1897	53	45
8	1.03024	1.02881	287	278	44	1.1975	1.19485	54	45
					45	1.2028	1.20005	55	45
9	1.03437	1.03290	294	284					
10	1.03853	1.03702	301	290	46	1.20805	1.2053	55	46
11	1.04271	1.04118	308	295	47	1.2134	1.2106	56	46
12	1.04692	1.04535	315	300	48	1.2187	1.2159	57	46
					49	1.2241	1.2212	57	47
13	1.05116	1.04955	323	307	50	1.2295	1.2266	58	47
14	1.05543	1.05378	330	313					
15	1.05972	1.05804	337	318	51	1.2349	1.2320	59	47
16	1.06405	1.06233	345	324	52	1.2404	1.2374	59	48
					53	1.2459	1.2429	60	48
17	1.06840	1.06664	352	329	54	1.2514	1.2484	60	48
18	1.07278	1.07098	360	336	55	1.2570	1.2539	61	49
19	1.07719	1.07535	367	341					
20	1.08162	1.07975	375	347	56	1.2626	1.2595	62	49
			$\times 10^{-6}$	$\times 10^{-6}$	57	1.2682	1.2651	62	49
21	1.08606	1.0842	38	35	58	1.2739	1.2707	63	50
22	1.09055	1.0886	38	35	59	1.2796	1.2764	64	50
23	1.09507	1.0931	39	36					
24	1.09962	1.0976	40	36	60	1.2853	1.2821	64	50
25	1.10420	1.1022	41	37	61	1.2911	1.2878	65	50
					62	1.2969	1.2936	66	51
26	1.1088	1.10675	41	37	63	1.3027	1.2994	66	51
27	1.11345	1.11135	42	38					
28	1.1181	1.1160	43	38	64	1.3086	1.3052	67	51
29	1.1229	1.1207	43	39	65	1.3145	1.3111	67	51
30	1.1276	1.1254	44	39	66	1.3204	1.3170	68	51
					67	1.3263	1.3229	69	52
31	1.1324	1.13015	45	40					
32	1.1372	1.1349	46	40	68	1.3323	1.3289	69	52
33	1.14205	1.1397	46	40	69	1.3384	1.3349	70	52
34	1.1469	1.1446	47	41	70	1.3444	1.3409	70	52
35	1.15185	1.1495	48	41	71	1.3505	1.3470	71	53

TABLE 19.—*Corrections to readings of Brix hydrometers immersed in levulose solutions*

[The corrections at 20° C. were determined by referring the densities of levulose solutions of known concentration to the sucrose density tables of Plato. The corrections at other temperatures are the algebraic sum of the corrections at 20° C. and the temperature corrections for sucrose multiplied by the ratios of the expansion coefficients of levulose and sucrose. The hydrometer is assumed to be constructed of Jena 16 III glass. Compare B. S. Circular No. 19, p. 23.]

[Standardized for sucrose solutions at 20° C.]

Temperature °C.	Observed Brix														
	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
	Corrections														
18	−0.09	−0.16	−0.20	−0.26	−0.29	−0.30	−0.29	−0.29	−0.26	−0.22	−0.21	−0.09	+0.01	+0.12	+0.28
19	−.05	−.10	−.15	−.20	−.22	−.21	−.22	−.20	−.17	−.13	−.08	.00	+.10	+.21	+.38
20	.00	−.05	−.09	−.13	−.15	−.14	−.13	−.12	−.09	−.05	+.02	+.10	+.20	+.31	+.44
21	+.04	.00	−.02	−.06	−.08	−.05	−.04	−.04	−.01	+.05	+.08	+.20	+.30	+.42	+.56
22	+.10	+.06	+.03	+.01	−.01	+.02	+.04	+.05	+.06	+.13	+.22	+.30	+.40	+.52	+.65
23	+.16	+.12	+.10	+.07	+.08	+.10	+.13	+.13	+.17	+.23	+.32	+.40	+.51	+.62	+.76
24	+.21	+.19	+.17	+.15	+.16	+.19	+.21	+.23	+.27	+.33	+.42	+.50	+.61	+.73	+.87
25	+.27	+.25	+.25	+.23	+.23	+.27	+.30	+.32	+.36	+.41	+.50	+.59	+.70	+.82	+.96
26	+.33	+.32	+.31	+.30	+.33	+.35	+.38	+.41	+.46	+.52	+.60	+.70	+.81	+.93	+1.08
27	+.40	+.39	+.38	+.38	+.40	+.45	+.48	+.51	+.55	+.60	+.70	+.80	+.92	+1.04	+1.18
28	+.46	+.45	+.46	+.46	+.50	+.54	+.57	+.61	+.64	+.70	+.80	+.90	+1.02	+1.14	+1.29

TABLE 20.—*Refractive indices of levulose solutions*

[All data computed from weights in air with brass weights. Immersion readings are referable solely to the scale of arbitrary units proposed by Pulfrich (Zeit. angew. Chemie, p. 1186; 1899). According to this scale, 14.5=1.33300; 50.0=1.34650; and 100.0=1.36464]

Per cent	$n^{20°}_D$	Zeiss immersion reading 20°	$n^{25°}_D$	Zeiss immersion reading 25°	$\frac{-\Delta n}{\Delta t°}$	Per cent	$n^{20°}_D$	$n^{25°}_D$	$\frac{-\Delta n}{\Delta t°}$	Per cent	$n^{20°}_D$	$n^{25°}_D$	$\frac{-\Delta n}{\Delta t°}$
					$\times 10^{-6}$				$\times 10^{-6}$				$\times 10^{-6}$
0	1.33300	14.50	1.33252	13.25	96	32	1.38385	1.38297	175	64	1.4479	1.4467	24
1	3442	18.18	3393	16.90	98	33	8564	8476	177	65	501	489	24
2	3585	21.87	3535	20.58	100	34	8745	8655	180	66	524	512	24
3	3729	25.63	3678	24.29	102	35	8927	8836	183	67	547	535	24
4	3874	29.42	3822	28.05	104	36	9111	9018	185	68	569	557	24
5	4020	33.26	3967	31.87	106	37	9295	9201	188	69	592	580	24
6	4167	37.14	4113	35.71	108	38	9481	9386	190	70	615	602	24
7	4315	41.05	4260	39.61	110	39	9669	9573	192	71	638	625	24
8	4464	45.03	4408	43.53	112	40	9858	9760	195	72	661	648	24
9	4614	49.05	4557	47.53	115	41	1.40048	9949	197	73	684	672	25
10	4765	53.11	4707	51.54	117	42	0239	1.40140	199	74	708	695	25
11	4917	57.19	4857	55.57	119	43	0432	0331	202	75	731	719	25
12	5070	61.32	5009	59.68	121	44	0625	0524	204	76	755	742	25
13	5224	65.51	5162	63.81	123	45	0821	0718	206	77	779	766	25
14	5379	69.75	5316	68.00	125	46	1018	0914	208	78	803	790	25
15	5534	74.03	5470	72.25	127	47	1216	1111	210	79	827	814	25
16	5691	78.36	5626	76.56	129	48	1415	1309	213	80	851	838	25
17	5849	82.75	5783	80.92	132	49	1616	1509	214	81	875	862	25
18	6008	87.17	5942	85.28	135	50	1818	1710	216	82	900	887	25
19	6169	91.64	6102	89.71	137	51	2021	1912	218	83	924	912	25
20	6332	96.14	6262	94.17	139	52	2226	2117	219	84	949	936	25
21	6496	100.72	6425	98.71	142	53	2432	2322	221	85	974	961	25
22	6659	105.37	6588	103.31	146	54	2640	2528	223	86	999	986	25
23	6827	-------	6753	-------	148	55	2848	2736	224	87	1.5024	1.5011	25
24	6996	-------	6921	-------	151	56	3058	2945	228	88	049	036	25
25	7166	-------	7088	-------	154	57	3270	3156	228	89	074	062	25
26	7336	-------	7258	-------	157	58	3482	3368	229	90	100	087	25
27	7506	-------	7426	-------	161	59	3696	3581	231	91	126	113	26
28	7680	-------	7598	-------	164	60	3913	3797	232	92	151	139	26
29	7854	-------	7771	-------	166	61	4130	4014	233	93	177	165	26
30	8030	-------	7945	-------	169	62	4348	4232	235	94	203	191	25
31	8207	-------	8121	-------	172	63	4569	4451	236	95	230	217	25

TABLE 21.—*Corrections to be applied to saccharimetric readings of levulose solutions when a constant normal weight is used*

[Normal weight at 20° C. = 18.407 gm; normal weight at 25° C. = 19.003 gm]

Polarization	Correction		Polarization	Correction		Polarization	Correction	
	20° C.	25° C.		20° C.	25° C.		20° C.	25° C.
0	0.00	0.00	40	+0.54	+0.57	75	+0.44	+0.47
5	+.10	+.11	45	.56	.60	80	.38	.40
10	.19	.21	50	.57	.61	85	.30	.33
15	.28	.30	52	.58	.61	90	.21	.23
20	.35	.39	55	.57	.61	95	.11	.12
25	.42	.45	60	.56	.59	100	.00	.00
30	.47	.50	65	.53	.56	105	−.11	−.14
35	.51	.55	70	.50	.52	110	−.20	−.26

NOTE.—In order to avoid constant repetition of the negative sign, the polarizations of levulose are considered positive. The positive signs in the above table indicate that the negative polarizations of levulose are to be increased to higher negative values.

TABLE 22.—*Table of factors for Lane and Eynon's volumetric reducing sugar method*

The factor represents the number of mg sugar required to reduce 25 ml of Soxhlet reagent.

$$100 \times \frac{\text{factor}}{\text{titer}} = \text{mg sugar in 100 ml.}$$

[In the last three columns are titer corrections corresponding to experimentally determined factors which differ from the tabulated factors by 1, 2, and 3 units. When the experimental factor is greater than the tabulated, the correction is to be subtracted from the observed titer, and vice versa. This corrected titer is to be used with the tabulated factor]

Titer	Dextrose	10	20	30	40	Invert Sugar	60	70	80	90	Levulose	Titer corrections		
												1	2	3
15	120.2	120.9	121.6	122.2	122.9	123.6	124.4	125.1	125.9	126.6	127.4	0.12	0.24	0.37
16	120.2	120.9	121.6	122.2	122.9	123.6	124.4	125.1	125.9	126.6	127.4	.13	.26	.39
17	120.2	120.9	121.6	122.2	122.9	123.6	124.4	125.2	125.9	126.7	127.5	.14	.28	.41
18	120.2	120.9	121.6	122.3	123.0	123.7	124.5	125.2	126.0	126.7	127.5	.15	.30	.44
19	120.3	121.0	121.7	122.3	123.0	123.7	124.5	125.3	126.0	126.8	127.6	.15	.31	.46
20	120.3	121.0	121.7	122.4	123.1	123.8	124.6	125.3	126.1	126.8	127.6	.16	.33	.49
21	120.3	121.0	121.7	122.4	123.1	123.8	124.6	125.4	126.1	126.9	127.7	.17	.34	.51
22	120.4	121.1	121.8	122.5	123.2	123.9	124.7	125.4	126.2	126.9	127.7	.18	.36	.54
23	120.4	121.1	121.8	122.5	123.2	123.9	124.7	125.5	126.2	127.0	127.8	.19	.37	.56
24	120.5	121.2	121.9	122.6	123.3	124.0	124.8	125.5	126.3	127.0	127.8	.20	.39	.59
25	120.5	121.2	121.9	122.6	123.3	124.0	124.8	125.6	126.3	127.1	127.9	.20	.41	.61
26	120.6	121.3	122.0	122.7	123.4	124.1	124.9	125.6	126.4	127.1	127.9	.21	.42	.63
27	120.6	121.3	122.0	122.7	123.4	124.1	124.9	125.7	126.4	127.2	128.0	.22	.44	.66
28	120.7	121.4	122.1	122.8	123.5	124.2	125.0	125.7	126.5	127.2	128.0	.23	.45	.68
29	120.7	121.4	122.1	122.8	123.5	124.2	125.0	125.8	126.5	127.3	128.1	.24	.47	.71
30	120.8	121.5	122.2	122.9	123.6	124.3	125.1	125.8	126.6	127.3	128.1	.25	.49	.73
31	120.8	121.5	122.2	122.9	123.6	124.3	125.1	125.8	126.6	127.3	128.1	.25	.50	.76
32	120.8	121.5	122.2	123.0	123.7	124.4	125.2	125.9	126.7	127.4	128.2	.26	.52	.78
33	120.9	121.6	122.3	123.0	123.7	124.4	125.2	125.9	126.7	127.4	128.2	.27	.54	.80
34	120.9	121.6	122.3	123.1	123.8	124.5	125.3	126.0	126.8	127.5	128.3	.28	.55	.83
35	121.0	121.7	122.4	123.1	123.8	124.5	125.3	126.0	126.8	127.5	128.3	.29	.57	.85
36	121.0	121.7	122.4	123.2	123.9	124.6	125.4	126.1	126.9	127.6	128.4	.29	.59	.88
37	121.1	121.8	122.5	123.2	123.9	124.6	125.4	126.1	126.9	127.6	128.4	.30	.60	.90
38	121.2	121.9	122.6	123.3	124.0	124.7	125.5	126.2	127.0	127.7	128.5	.31	.62	.93
39	121.2	121.9	122.6	123.3	124.0	124.7	125.5	126.2	127.0	127.7	128.5	.32	.63	.95
40	121.2	121.9	122.6	123.4	124.1	124.8	125.6	126.3	127.1	127.8	128.6	.33	.65	.98
41	121.3	122.0	122.7	123.4	124.1	124.8	125.6	126.3	127.1	127.8	128.6	.33	.67	1.00
42	121.4	122.1	122.8	123.5	124.2	124.9	125.6	126.4	127.1	127.9	128.6	.34	.68	1.02
43	121.4	122.1	122.8	123.5	124.2	124.9	125.7	126.4	127.2	127.9	128.7	.35	.70	1.05
44	121.5	122.2	122.9	123.6	124.3	125.0	125.7	126.5	127.2	128.0	128.7	.36	.72	1.07
45	121.5	122.2	122.9	123.6	124.3	125.0	125.8	126.5	127.3	128.0	128.8	.37	.73	1.10
46	121.6	122.3	123.0	123.7	124.4	125.1	125.8	126.6	127.3	128.1	128.8	.37	.75	1.12
47	121.6	122.3	123.0	123.7	124.4	125.1	125.9	126.6	127.4	128.1	128.9	.38	.76	1.15
48	121.7	122.4	123.1	123.8	124.5	125.2	125.9	126.7	127.4	128.2	128.9	.39	.78	1.17
49	121.7	122.4	123.1	123.8	124.5	125.2	126.0	126.7	127.5	128.2	129.0	.40	.80	1.20
50	121.8	122.5	123.2	123.9	124.6	125.3	126.0	126.8	127.5	128.3	129.0	.41	.81	1.22

TABLE 23.—*Copper-levulose equivalents according to Jackson and Mathews's modification of Nyns's selective method for levulose*

[All data expressed in milligrams]

Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose
1	0.6	40	13.9	79	25.1	118	36.0	157	46.6	196	56.8	235	67.9	274	80.4
2	1.1	41	14.2	80	25.4	119	36.2	158	46.9	197	57.1	236	68.2	275	80.7
3	1.6	42	14.5	81	25.7	120	36.5	159	47.1	198	57.3	237	68.5	276	81.0
4	2.1	43	14.8	82	25.9	121	36.8	160	47.4	199	57.6	238	68.8	277	81.4
5	2.5	44	15.1	83	26.2	122	37.1	161	47.7	200	57.9	239	69.1	278	81.7
6	2.9	45	15.4	84	26.5	123	37.3	162	47.9	201	58.1	240	69.4	279	82.0
7	3.3	46	15.7	85	26.8	124	37.6	163	48.2	202	58.4	241	69.7	280	82.4
8	3.7	47	16.0	86	27.0	125	37.9	164	48.4	203	58.7	242	70.0	281	82.7
9	4.1	48	16.3	87	27.3	126	38.2	165	48.7	204	58.9	243	70.3	282	83.1
10	4.5	49	16.6	88	27.6	127	38.5	166	49.0	205	59.2	244	70.7	283	83.4
11	4.8	50	16.8	89	27.9	128	38.7	167	49.2	206	59.4	245	71.0	284	83.8
12	5.1	51	17.1	90	28.1	129	39.0	168	49.5	207	59.7	246	71.3	285	84.1
13	5.5	52	17.4	91	28.4	130	39.3	169	49.7	208	60.0	247	71.6	286	84.4
14	5.9	53	17.7	92	28.7	131	39.6	170	50.0	209	60.3	248	71.9	287	84.8
15	6.2	54	18.0	93	29.0	132	39.9	171	50.2	210	60.6	249	72.2	288	85.1
16	6.5	55	18.3	94	29.2	133	40.1	172	50.5	211	60.9	250	72.5	289	85.5
17	6.9	56	18.6	95	29.5	134	40.4	173	50.8	212	61.1	251	72.8	290	85.9
18	7.2	57	18.9	96	29.8	135	40.7	174	51.0	213	61.4	252	73.1	291	86.2
19	7.6	58	19.1	97	30.1	136	40.9	175	51.3	214	61.7	253	73.5	292	86.6
20	7.9	59	19.4	98	30.4	137	41.2	176	51.5	215	62.0	254	73.8	293	86.9
21	8.2	60	19.7	99	30.7	138	41.5	177	51.8	216	62.3	255	74.1	294	87.3
22	8.5	61	20.0	100	30.9	139	41.7	178	52.1	217	62.6	256	74.4	295	87.6
23	8.9	62	20.3	101	31.2	140	42.0	179	52.3	218	62.9	257	74.7	296	88.0
24	9.2	63	20.6	102	31.5	141	42.3	180	52.6	219	63.2	258	75.1	297	88.4
25	9.5	64	20.9	103	31.8	142	42.6	181	52.8	220	63.4	259	75.4	298	88.7
26	9.8	65	21.2	104	32.1	143	42.8	182	53.1	221	63.7	260	75.7	299	89.1
27	10.1	66	21.4	105	32.3	144	43.1	183	53.4	222	64.0	261	76.0	300	89.5
28	10.4	67	21.7	106	32.6	145	43.4	184	53.6	223	64.3	262	76.4	301	89.8
29	10.7	68	22.0	107	32.9	146	43.7	185	53.9	224	64.6	263	76.7	302	90.2
30	11.0	69	22.2	108	33.2	147	43.9	186	54.2	225	64.9	264	77.0	303	90.5
31	11.3	70	22.5	109	33.5	148	44.2	187	54.4	226	65.2	265	77.4	304	90.9
32	11.6	71	22.8	110	33.7	149	44.5	188	54.7	227	65.5	266	77.7	305	91.3
33	11.9	72	23.1	111	34.0	150	44.7	189	54.9	228	65.8	267	78.1	306	91.7
34	12.2	73	23.4	112	34.3	151	45.0	190	55.2	229	66.1	268	78.4	307	92.0
35	12.5	74	23.7	113	34.6	152	45.3	191	55.5	230	66.4	269	78.7	308	92.4
36	12.8	75	24.0	114	34.8	153	45.6	192	55.7	231	66.7	270	79.0	309	92.8
37	13.1	76	24.2	115	35.1	154	45.8	193	56.0	232	67.0	271	79.4	310	93.2
38	13.4	77	24.5	116	35.4	155	46.1	194	56.3	233	67.3	272	79.7	311	93.5
39	13.7	78	24.8	117	35.7	156	46.4	195	56.5	234	67.6	273	80.0	312	93.9

Example illustrating the use of Table 24 (see discussion, p. 433).—Assume that a solution of levulose and dextrose polarized at 20° C. −43.8° S., and that 5 ml of this solution diluted to 100 ml gave a Lane and Eynon titration of 26.18 ml when the correction for the titration factor is zero. Then

$$D = 100/5 = 20$$

and

$$\frac{PT}{D} = -\frac{43.8 \times 26.18}{20} = -57.3.$$

By Table 24 the approximate ratio is 89.8 per cent, and the correction factor, f, is −0.80. The correction is

$$\frac{f \times D}{T} = -\frac{0.80 \times 20}{26.18} = -0.6$$

and the true ratio is

$$89.8 - 0.6 = 89.2$$

The concentration of total sugar is calculated in the usual way from the titer

$$\frac{100\,F}{T} = \frac{100 \times 127.0}{26.18} = 485.1 \text{ mg per 100 ml of solution titrated}$$

The concentration in the polarized solution is

$$0.4851 \times 20 = 9.702 \text{ g per 100 ml}$$

and levulose is

$$9.702 \times 89.2 \text{ per cent} = 8.654 \text{ g per 100 ml.}$$

TABLE 24.—*Ratio of levulose to total sugar from Lane and Eynon titration and polarization by Mathews formula*

[The table gives the per cent ratio (R) of levulose to total reducing sugar calculated from the Lane and Eynon titration and the direct polarization at 20° C. P is the polarization in °S; T is the corrected Lane and Eynon titer; D is the number of volumes to which one volume of the solution polarized was diluted for the titration; and f is the factor used for correcting the per cent ratio found in the table. This correction is given by

$$\frac{f \times D}{T},$$

and is to be added algebraically.

The table can be used when the polarization is made at a temperature other than 20° C. by using the temperature coefficient, $\Delta R/\Delta t°$. When the temperature is $t°$, the correction is $\frac{\Delta R}{\Delta t°}(t°-20°)$, and is to be added algebraically to the ratio.]

$\frac{P \cdot T}{D}$	$T=15$	$T=25$	$T=35$	$T=45$	f	$\frac{\Delta R}{\Delta t°}$	$\frac{P \cdot T}{D}$	$T=15$	$T=25$	$T=35$	$T=45$	f	$\frac{\Delta R}{\Delta t°}$	$\frac{P \cdot T}{D}$	$T=15$	$T=25$	$T=35$	$T=45$	f	$\frac{\Delta R}{\Delta t°}$
37	−0.6	−0.4	−0.3	−0.2	0.29	0	1	34.0	34.0	34.0	34.0	−0.13	0.15	−35	68.6	68.4	68.3	68.2	−0.54	0.30
36	+0.4	+0.5	+0.7	+0.8	.28	0	0	35.0	35.0	35.0	35.0	−.14	.15	−36	69.5	69.4	69.3	69.2	−.56	.30
35	1.4	1.5	1.6	1.7	.27	0.01	−1	35.9	35.9	35.9	35.9	−.15	.16	−37	70.5	70.3	70.2	70.1	−.57	.31
34	2.3	2.4	2.6	2.7	.26	.01	−2	36.9	36.9	36.9	36.9	−.16	.16	−38	71.4	71.3	71.2	71.1	−.58	.31
33	3.3	3.4	3.5	3.6	.24	.02	−3	37.8	37.8	37.8	37.8	−.17	.17	−39	72.4	72.3	72.4	72.0	−.59	.32
32	4.2	4.4	4.5	4.6	.23	.02	−4	38.8	38.8	38.8	38.8	−.18	.17	−40	73.4	73.2	73.1	73.0	−.60	.32
31	5.2	5.3	5.4	5.5	.22	.02	−5	39.8	39.8	39.7	39.7	−.20	.17	−41	74.3	74.2	74.1	73.9	−.61	.32
30	6.2	6.3	6.4	6.5	.21	.03	−6	40.7	40.7	40.7	40.7	−.21	.18	−42	75.3	75.1	75.0	74.9	−.63	.33
29	7.1	7.2	7.3	7.4	.20	.03	−7	41.7	41.7	41.6	41.6	−.22	.18	−43	76.2	76.1	76.0	75.8	−.64	.33
28	8.1	8.2	8.3	8.4	.19	.04	−8	42.6	42.6	42.6	42.6	−.23	.19	−44	77.2	77.0	76.9	76.8	−.65	.34
27	9.0	9.1	9.2	9.3	.18	.04	−9	43.6	43.6	43.6	43.5	−.24	.19	−45	78.2	78.0	77.9	77.7	−.66	.34
26	10.0	10.1	10.2	10.3	.16	.04	−10	44.6	44.5	44.5	44.5	−.25	.19	−46	79.1	79.0	78.8	78.7	−.67	.34
25	11.0	11.1	11.1	11.2	.15	.05	−11	45.5	45.5	45.5	45.4	−.27	.20	−47	80.1	79.9	79.8	79.6	−.68	.35
24	11.9	12.0	12.1	12.2	.14	.05	−12	46.5	46.4	46.4	46.4	−.28	.20	−48	81.0	80.9	80.7	80.6	−.69	.35
23	12.9	13.0	13.1	13.1	.13	.06	−13	47.4	47.4	47.4	47.3	−.29	.21	−49	82.0	81.8	81.7	81.5	−.71	.36
22	13.8	13.9	14.0	14.1	.12	.06	−14	48.4	48.4	48.3	48.3	−.30	.21	−50	83.0	82.8	82.6	82.5	−.72	.36
21	14.8	14.9	15.0	15.0	.11	.07	−15	49.4	49.3	49.3	49.2	−.31	.22	−51	83.9	83.7	83.6	83.4	−.73	.37
20	15.8	15.8	15.9	16.0	.09	.07	−16	50.3	50.3	50.2	50.2	−.32	.22	−52	84.9	84.7	84.5	84.4	−.74	.37
19	16.7	16.8	16.9	16.9	.08	.07	−17	51.3	51.2	51.2	51.1	−.34	.22	−53	85.8	85.7	85.5	85.3	−.75	.37
18	17.7	17.7	17.8	17.9	.07	.08	−18	52.2	52.2	52.1	52.1	−.35	.23	−54	86.8	86.6	86.4	86.3	−.76	.38
17	18.6	18.7	18.8	18.8	.06	.08	−19	53.2	53.1	53.1	53.0	−.36	.23	−55	87.8	87.6	87.4	87.2	−.78	.38
16	19.6	19.6	19.7	19.8	.05	.09	−20	54.2	54.1	54.0	54.0	−.37	.24	−56	88.7	88.5	88.3	88.2	−.79	.39
15	20.6	20.6	20.7	20.7	.04	.09	−21	55.1	55.0	55.0	54.9	−.38	.24	−57	89.7	89.5	89.3	89.1	−.80	.39
14	21.5	21.6	21.6	21.7	.02	.10	−22	56.1	56.0	56.0	55.9	−.39	.24	−58	90.6	90.4	90.3	90.1	−.81	.39
13	22.5	22.5	22.6	22.6	.01	.10	−23	57.0	57.0	56.9	56.8	−.40	.25	−59	91.6	91.4	91.2	91.0	−.82	.40
12	23.4	23.5	23.5	23.6	.00	.10	−24	58.0	57.9	57.9	57.8	−.42	.25	−60	92.6	92.3	92.2	92.0	−.83	.40
11	24.4	24.4	24.5	24.5	−.01	.11	−25	59.0	58.9	58.8	58.7	−.43	.26	−61	93.5	93.3	93.1	92.9	−.85	.41
10	25.4	25.4	25.4	25.5	−.02	.11	−26	59.9	59.8	59.8	59.7	−.44	.26	−62	94.5	94.3	94.1	93.9	−.86	.41
9	26.3	26.4	26.4	26.4	−.03	.12	−27	60.9	60.8	60.7	60.6	−.45	.27	−63	95.4	95.2	95.0	94.8	−.87	.42
8	27.3	27.3	27.3	27.4	−.05	.12	−28	61.8	61.7	61.7	61.6	−.46	.27	−64	96.4	96.2	96.0	95.8	−.88	.42
														−65	97.4	97.1	96.9	96.7	−.89	.42

9	26.3	26.4	26.4	26.4	−.03	.12	−27	60.9	60.8	60.7	60.6	−.45	.27	−63	95.4	95.2	95.0	94.8	−.87	.42
8	27.3	27.3	27.3	27.4	−.05	.12	−28	61.8	61.7	61.7	61.6	−.46	.27	−64	96.4	96.2	96.0	95.8	−.88	.42
7	28.2	28.3	28.3	28.3	−.06	.12	−29	62.8	62.7	62.6	62.5	−.47	.27	−65	97.4	97.1	96.9	96.7	−.89	.42
6	29.2	29.2	29.3	29.3	−.07	.13	−30	63.8	63.7	63.6	63.5	−.49	.28	−66	98.3	98.1	97.9	97.7	−.90	.43
5	30.2	30.2	30.2	30.2	−.08	.13	−31	64.7	64.6	64.5	64.4	−.50	.28	−67	99.3	99.0	98.8	98.6	−.92	.43
4	31.1	31.1	31.2	31.2	−.09	.14	−32	65.7	65.6	65.5	65.4	−.51	.29	−68	100.2	100.0	99.8	99.6	−.93	.44
3	32.1	32.1	32.1	32.1	−.10	.14	−33	66.6	66.5	66.4	66.3	−.52	.29	−69	101.2	101.0	100.7	100.5	−.94	.44
2	33.0	33.0	33.1	33.1	−.11	.14	−34	67.6	67.5	67.4	67.3	−.53	.29	−70	102.2	101.9	101.7	101.5	−.95	.44

Example illustrating the use of Table 25 (see discussion, p. 434).—Assume that a solution of levulose and dextrose gave a Lane and Eynon titer of 25.89 ml and that 20 ml of the same solution precipitated 247.3 mg of copper by the modified Nyns method. The original solution then contained by Table 23 $\frac{100\times 71.7}{20}=358.5$ mg of apparent levulose per 100 ml. Then

$$\frac{T\times l}{100}=\frac{25.89\times 358.5}{100}=92.8$$

Referring to Table 25 we find opposite this product and under $T=25$ the true ratio of levulose to total sugar to be 71.5 per cent. Lane and Eynon's factor is 125.7 and the total sugar per 100 ml is $\frac{125.7}{25.89}=485.5$ mg, of which 71.5 per cent = 347.1 mg is levulose and 138.4 mg is dextrose.

TABLE 25.—*Ratio of levulose to total sugar from Lane and Eynon titration and Nyns "apparent" levulose*

$\frac{T\times l}{100}$	T=15	T=25	T=35	T=45	$\frac{T\times l}{100}$	T=15	T=25	T=35	T=45	$\frac{T\times l}{100}$	T=15	T=25	T=35	T=45
11	1.2	1.2	1.1	1.1	50	35.6	35.4	35.2	35.0	89	68.5	68.3	68.1	67.8
12	2.1	2.1	2.0	2.0	51	36.5	36.3	36.1	35.9	90	69.3	69.1	68.9	68.6
13	3.0	3.0	2.9	2.9	52	37.3	37.2	36.9	36.7	91	70.2	70.0	69.7	69.4
14	3.9	3.8	3.8	3.7	53	38.2	38.0	37.8	37.6	92	71.0	70.8	70.6	70.3
15	4.8	4.7	4.7	4.6						93	71.9	71.7	71.4	71.1
					54	39.1	38.9	38.6	38.4					
16	5.7	5.6	5.6	5.5	55	39.9	39.7	39.5	39.3	94	72.7	72.5	72.3	72.0
17	6.5	6.5	6.4	6.4	56	40.8	40.6	40.3	40.1	95	73.5	73.3	73.1	72.8
18	7.4	7.4	7.3	7.3	57	41.7	41.5	41.2	40.9	96	74.3	74.2	73.9	73.6
19	8.3	8.2	8.2	8.1	58	42.5	42.3	42.1	41.8	97	75.2	75.0	74.7	74.4
20	9.2	9.1	9.1	9.0						98	76.0	75.8	75.6	75.3
					59	43.4	43.2	42.9	42.6					
21	10.1	10.0	10.0	9.9	60	44.2	44.0	43.8	43.5	99	76.8	76.6	76.4	76.1
22	11.0	10.9	10.9	10.8	61	45.0	44.8	44.6	44.3	100	77.6	77.4	77.2	76.9
23	11.9	11.8	11.8	11.7	62	45.9	45.7	45.5	45.2	101	78.5	78.2	78.0	77.7
24	12.8	12.7	12.6	12.5	63	46.7	46.5	46.3	46.0	102	79.3	79.0	78.8	78.5
										103	80.1	79.9	79.6	79.3
25	13.7	13.6	13.5	13.4	64	47.6	47.4	47.2	46.9					
26	14.5	14.4	14.3	14.2	65	48.4	48.2	48.0	47.7	104	81.0	80.7	80.4	80.1
27	15.4	15.3	15.2	15.1	66	49.3	49.0	48.8	48.5	105	81.8	81.5	81.2	80.9
28	16.3	16.2	16.1	16.0	67	50.1	49.9	49.7	49.4	106	82.6	82.3	82.0	81.7
					68	51.0	50.8	50.6	50.2	107	83.5	83.2	82.8	82.5
29	17.2	17.1	17.0	16.9						108	84.3	84.0	83.6	83.3
30	18.1	18.0	17.9	17.8	69	51.8	51.6	51.4	51.1					
31	19.0	18.9	18.7	18.6	70	52.7	52.5	52.2	51.9	109	85.1	84.8	84.4	84.1
32	19.9	19.8	19.6	19.5	71	53.5	53.3	53.1	52.8	110	85.9	85.6	85.2	84.9
33	20.8	20.6	20.5	20.4	72	54.3	54.1	53.9	53.6	111	86.7	86.4	86.0	85.7
					73	55.2	55.0	54.7	54.4	112	87.5	87.2	86.8	86.5
34	21.6	21.5	21.4	21.3						113	88.3	88.0	87.6	87.3
35	22.5	22.4	22.3	22.2	74	56.0	55.8	55.6	55.3					
36	23.4	23.3	23.2	23.1	75	56.8	56.6	56.4	56.1	114	89.1	88.8	88.4	88.1
37	24.3	24.2	24.0	23.9	76	57.7	57.5	57.2	56.9	115	90.0	89.6	89.3	88.9
38	25.2	25.1	24.9	24.8	77	58.5	58.3	58.1	57.8	116	90.8	90.4	90.1	89.7
					78	59.4	59.2	58.9	58.6	117	91.6	91.3	91.0	90.6
39	26.1	26.0	25.8	25.7						118	92.4	92.1	92.8	91.4
40	26.9	26.8	26.6	26.5	79	60.2	60.0	59.8	59.5					
41	27.8	27.7	27.5	27.4	80	61.1	60.9	60.6	60.3	119	93.2	92.9	92.6	92.2
42	28.7	28.6	28.4	28.3	81	61.9	61.7	61.4	61.1	120	94.0	93.7	93.4	93.0
43	29.5	29.4	29.2	29.1	82	62.8	62.5	62.3	62.0	121	94.8	94.5	94.2	93.8
					83	63.6	63.3	63.1	62.8	122	95.6	95.3	95.0	94.6
44	30.4	30.3	30.1	30.0										
45	31.3	31.2	31.0	30.8	84	64.4	64.2	63.9	63.6	123	96.4	96.1	95.8	95.4
46	32.2	32.0	31.9	31.7	85	65.2	65.0	64.8	64.5	124	97.3	97.0	96.6	96.2
47	33.0	32.9	32.7	32.5	86	66.0	65.8	65.6	65.3	125	98.1	97.8	97.4	97.0
48	33.9	33.8	33.6	33.4	87	66.9	66.7	66.4	66.1	126	98.9	98.6	98.2	97.8
					88	67.7	67.5	67.2	66.9	127	99.7	99.4	99.0	98.6
49	34.8	34.6	34.4	34.2										

WASHINGTON, January 27, 1932.